

Oscillator Strengths and Excited State Lifetimes in Metallic Hydrides and Oxides

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1 Introduction

It is really impressive to see the amount of information astrophysicists have been able to extract from the analysis of that faint glimmering light that stars send to tell us about them. The main piece of this analysis consists in dispersing the light to get the spectrum, that is to say intensity versus wavenumbers. From the measurements of wavenumbers it is possible to identify the atomic and molecular species from comparison with high-resolution laboratory spectroscopic data. Once the constituents have been identified, models can be constructed in order to simulate the metabolism of circumstellar atmospheres. In such models a crucial point is the abundance of the identified atomic and molecular constituents.

In principle abundances can be deduced from intensities since intensities are proportional to them. But actually intensities are also proportional to something that is often poorly known, sometimes not at all, especially in the case of molecules. That "something" reflects the propensity of a given transition to occur: it is the (squared) transition dipole moment (or higher multipole moments when necessary) or, in an initiated language, quantities associated with this moment called oscillator strengths, Einstein coefficients and excited state lifetimes. The purpose of this chapter is to review oscillator strengths and lifetimes for a class of molecules that are important in cool stars, the metallic oxides and hydrides, a class for which much information remains to be gained if one wants to deduce quantitatively reliable values of abundances from intensities. In the present status of knowledge, it is often necessary to assume more or less reasonable values for the unknown oscillator strengths. Certainly we are now gratifyingly far from the drastic assumptions of the first determinations of stellar abundances in which, in the lack of transition probability data, it was assumed as a stopgap that all transitions of all molecules had equal oscillator strengths (Russel 1934). The correct way to proceed requires a knowledge of accurate, or at least approximate, values of molecular transition probabilities. Unfortunately, as exemplified in the following, the situation is still far from being yet satisfactory in that matter.

The characteristics of stellar light are linked to the well-known theory of the

dynamical behaviour of quantum states of material systems. Briefly it can be said that when photons fall on a material medium, gaseous, liquid or solid, they can be absorbed, i.e. annihilated, by the molecules in this medium if they are resonant with one of the numerous rovibronic transitions between an initially populated state i (for instance the ground state) and an excited (discrete or not) state j of the molecules. To allow for energy conservation, the absorption of optical radiation is accompanied by the promotion of the molecule into this excited state j :



where ν_{ij} is the wavenumber of the i - j transition.

Once the molecule is in the excited state j , three kinds of processes can induce the depopulation of this state. The first one is stimulated emission that is usually small in the visible under LTE conditions. As it is described by the same radiative quantities as absorption, it need not be considered further. The second one is spontaneous emission towards any accessible i' level (among which the i level) lying lower than the excited state j , with emission of a resonant photon according to:



The third de-excitation process is non-radiative decay, a denomination that in fact covers many depopulation mechanisms, internal mechanisms, such as dissociation, predissociation, autoionisation, or external mechanisms, i.e. involving other molecules, such as collisional transfer or quenching.

2 Radiative Properties: Definitions

The absorption and emission processes are most interesting to astrophysicists: since direct measurements of stellar properties in the stellar environment are obviously out of the question, practically all the information collected about stars has been provided by achieving spectral analysis of the absorption by photospheres of the continuum emitted by the stellar cores and, to a somewhat lesser extent, of the re-emission of light by these absorbing photospheres.

An absolute intensity is defined as the energy flux emitted per second in emission and as the decrease in the energy flux per second in absorption. It is proportional to the density number of the emitting or absorbing species, to the energy $hc\nu$ of the emitted or absorbed photons and to the transition probability of the process.

As said above, transition probabilities and, as a consequence, absolute intensities of radiative effects are governed by the value of a central quantity: the square of the transition moment. Since the vast majority of the transitions of interest are dipole-allowed ones we restrict the discussion to the dipole transition moment between states i and j . It is defined as:

$$\mu_{ij} = \langle i | \sum_{\alpha} q_{\alpha} \vec{r}_{\alpha} | j \rangle \quad (3)$$

where the summation runs over all the charges q_α of the system at positions \vec{r}_α and $|i\rangle$ and $|j\rangle$ are two rovibronic states. Extension to higher multipole radiation is straightforward though somewhat cumbersome.

Now it often happens that the electronic part of the wavefunction can be separated from the nuclear (rotational and vibrational) part. This is known as the Born-Oppenheimer (B.O.) approximation (1927). In the B.O. approximation, the rovibronic transition moment is given by:

$$\mu_{ij} = \langle v'' J'' | \mathcal{R}_e(R) | v' J' \rangle \quad (4)$$

where $\mathcal{R}_e(R)$ is the electronic transition dipole moment, a function of the inter-nuclear distance; the ' and '' signs refer to the upper and lower electronic states, respectively. Moreover, since the rotational part of the wavefunction depends only on angles, μ_{ij} factorizes into

$$\mu_{ij} = \mu_{v'v''} S_{j'j''} \quad (5)$$

in which $S_{j'j''}$ is the rotational strength or Hönl-London factor of the transition, a simple function of the rotational quantum numbers that can be handled by conventional spherical tensor techniques. The $\mu_{v'v''}$ element is the vibronic transition moment:

$$\mu_{v'v''} = \langle v'' | \mathcal{R}_e(R) | v' \rangle \quad (6)$$

The $\mu_{v'v''}$ vibronic transition moment is typical of each transition and is the quantity to be focused on in the following. If the $\mathcal{R}_e(R)$ electronic transition moment is constant or if it varies linearly with R over the region where the vibrational wavefunctions are non-negligible, it is possible to simplify further the expression of the vibronic moment that becomes:

$$\mu_{v'v''} = \mathcal{R}_e(\overline{r'v''}) \langle v' | v'' \rangle \quad (7)$$

$\overline{r'v''}$ is a particular separation characteristic of the v', v'' couple and called their r -centroid (Nicholls 1969); $\langle v' | v'' \rangle$ is the vibrational overlap, the square of which is the well-known Franck-Condon factor. This factorization bears the name of Franck-Condon approximation.

In fact, intensities of molecular transitions are seldom characterized by their transition moments. Instead of these moments several inter-related quantities are introduced depending on whether photon or energy flux is detected and whether absorption or emission is considered. Thus for the case of absorption measured by a decrease in photon flux the transition rate is given by:

$$dN_{v'}/dt = -B_{v''v'} u_\nu N_{v'} \quad (8)$$

where u_ν is the differential energy density of the radiation field at wavenumber $\nu_{v'v''}$. The decrease in photon flux is expressed in terms of the (vibronic) Einstein coefficient in absorption:

$$B_{v''v'} = |\mu_{v'v''}|^2 2\pi^2 / 3h^2 \epsilon_0 c \quad (9)$$

i.e, numerically, for μ in Debye units and u_ν in $\text{J}/(\text{m}^3\text{cm}^{-1})$:

$$B_{\nu''\nu'}(\text{in } \text{J}^{-1}\text{m}^3\text{cm}^{-1}\text{s}^{-1}) = 4.056 \times 10^{17} |\mu_{\nu''\nu'}|^2 \tag{10}$$

Note that $B_{\nu''\nu'}$ is frequency independent. Note also that for $\Sigma \rightarrow \Pi$ transitions and for them only, μ should be replaced by $\sqrt{2}\mu$ in this formula and each time it appears in all others that follow (Whiting et al. 1980). For absorption measurements by a decrease in energy flux, the absolute intensity is proportional to the first power of the wavenumber and it is currently expressed in terms of the absorption oscillator strength $f_{\nu''\nu'}$:

$$f_{\nu''\nu'} = \nu_{\nu''\nu'} |\mu_{\nu''\nu'}|^2 16\pi^2 m_e c / 3h^2 e^2 \tag{11}$$

i.e, numerically, for μ in Debye units and ν in cm^{-1} ,

$$f_{\nu''\nu'} = 4.703 \times 10^{-7} \nu_{\nu''\nu'} |\mu_{\nu''\nu'}|^2 \tag{12}$$

Note that $f_{\nu''\nu'}$ is dimensionless. It can be shown from sum rules that its maximum value is unity, a value that would correspond to a “fully allowed” transition that leaves nothing for others.

Alternatively the absorption lineshape can be described in terms of so-called absorption cross-sections $\sigma_{\nu''\nu'}$ that lead, when integrated over wavenumbers, to the integrated cross-section:

$$\sigma_{\nu''\nu'}^0 = (4\pi^2 e^2 / m_e \epsilon_0) f_{ij} \tag{13}$$

i.e. numerically,

$$\sigma_{\nu''\nu'}^0(\text{in } \text{cm}^2) = 4.162 \times 10^{-19} \nu_{\nu''\nu'} |\mu_{\nu''\nu'}|^2 \tag{14}$$

The microscopic absorption cross-section $\sigma(\nu)$ is simply related to the macroscopic absorption coefficient $K(\nu)$ of the exponential Beer-Lambert law for absorption through the density number $N_{\nu''}$: $K(\nu) = N_{\nu''} \sigma(\nu)$

For emission over a single transition, from an excited level down to a lower-lying one, it is customary to introduce the spontaneous emission probability in photon flux detection as another Einstein coefficient:

$$A_{\nu''\nu'} = \nu_{\nu''\nu'}^3 |\mu_{\nu''\nu'}|^2 16\pi^2 / 3h\epsilon_0 \tag{15}$$

i.e. numerically, with the above unit conventions (ν in cm^{-1} and μ in Debye):

$$A_{\nu''\nu'}(\text{in } \text{s}^{-1}) = 3.137 \times 10^{-7} \nu_{\nu''\nu'}^3 |\mu_{\nu''\nu'}|^2 \tag{16}$$

Note the ν^3 dependence of $A_{\nu''\nu'}$. The spontaneous emission absolute intensity of the $\nu' \rightarrow \nu''$ transition, i.e. the energy flux emitted per unit volume of the source per second on this transition, is therefore proportional to the fourth power of the wavenumber:

$$I_{\nu''\nu'}(\text{in } \text{Wm}^{-3}) = N_{\nu'} h c \nu_{\nu''\nu'} A_{\nu''\nu'} = N_{\nu'} \nu_{\nu''\nu'}^4 |\mu_{\nu''\nu'}|^2 16\pi^2 c / 3\epsilon_0 \tag{17}$$

However, the global spontaneous emission from a level v' takes place towards all the lower-lying v'' levels, so that the depopulation rate of this level is a sum over all the possible transitions:

$$dN_{v'}/dt = -\left(\sum_{v''} A_{v'v''}\right)N_{v'} \quad (18)$$

It follows that the population of the upper state decreases exponentially with a time constant called the radiative lifetime of the excited vibronic level:

$$\tau_{v'} = \left(\sum_{v''} A_{v'v''}\right)^{-1} \quad (19)$$

Thus, in general, measuring the lifetime of an excited level does not lead to state-to-state transition moments but instead to a global value. However, as discussed later, there may be favourable situations in which rough values of transition moments can be extracted from lifetimes.

Before going further, it should be again recalled that all the constants considered above have been defined for ν standing for wavenumber, not frequency. As a general rule the problem of unities and that of statistical weight factors have led for long to considerable misleading in the problem of conversion between band strengths, oscillator strengths, transition probabilities and radiative lifetimes (Nicholls & Stewart 1962; Tatum 1967; Schadee 1967, 1971, 1978; Brown et al. 1976; Kuzmenko et al. 1979; Kuznetsova et al. 1974, 1980; Whiting 1972; Whiting & Nicholls 1974). Today this problem is definitely overcome since the recommendations given in the central paper by Whiting et al. (1980) seem to have been universally adopted, including for radiative lifetimes (Larsson 1983). The reader should refer to the latter two papers for details.

3 Effects of Perturbations and Predissociations

When the Born-Oppenheimer model holds, i.e. when electronic states are isolated from each others, all the rovibronic levels of a given electronic state have nearly identical lifetimes and all oscillator strengths between rovibronic levels of two electronic states follow regular laws: they differ because of different Franck-Condon factors but they correspond to the same (R) electronic transition moment. This is not always so simple, however, and defects to the B.O. approximation frequently appear. In such cases, the actual vibronic state j becomes a mixing of two (or more) quasi-degenerate B.O. states. The coupling that can induce such a mixing may have various origins: for example, kinetic, spin-orbit, Coriolis, or hyperfine interactions. This effect bears the generic name of perturbation. Perturbations are reviewed in full details in an excellent book by Lefebvre-Brion & Field (1986). The name of perturbation is more specifically reserved to the interaction of a bound state with another bound state. For a bound state perturbed by a free state of the continuum, one usually speaks of

predissociation when the bound level lies above the dissociation limit of a lower-lying electronic state, or of preionisation when it lies above the ionisation limit of the molecule.

A bound-bound perturbation is experimentally observed as both shifts in the positions of spectroscopic lines and drastic changes in the line intensities and lifetimes compared to some regular evolutions that would be observed in the absence of the perturber. We are concerned here by intensities and lifetimes and from this point of view two cases may be distinguished according to the radiative nature of the perturber. If the perturber is a metastable state $|m\rangle$, i.e. a state that cannot radiate towards lower states in the B.O. approximation because its transition moment towards these states is zero, the squared transition moment of the $|j\rangle$ perturbed state to the $|i\rangle$ state becomes:

$$|\langle j^{pert}|\mu|i\rangle|^2 = |\{\alpha\langle j| + (1 - \alpha^2)^{1/2}\langle m|\}\mu|i\rangle|^2 = \alpha^2|\mu_{ij}|^2 \quad (20)$$

Since the α coefficient is smaller than unity, the oscillator strengths and the Einstein coefficients of the transition are reduced by a factor α^2 . In the same way, assuming a single electronic channel depopulation, that to state i , the lifetime of the j level is lengthened by a factor $1/\alpha^2$ while the perturber, which had normally an "infinite" radiative lifetime, becomes able to radiate. To summarize, perturbation of a vibronic level j by a metastable state produces an intensity borrowing and an increase of lifetime.

Now, if the perturber, denoted $|r\rangle$, is also a radiative state (unperturbed lifetime τ_r), the (squared) transition moment to state i is:

$$\begin{aligned} |\langle j^{pert}|\mu|i\rangle|^2 &= |\alpha\langle j|\mu|i\rangle + (1 - \alpha^2)^{1/2}\langle r|\mu|i\rangle|^2 \\ &= \alpha^2|\mu_{ij}|^2 + (1 - \alpha^2)|\mu_{ri}|^2 + 2\alpha(1 - \alpha^2)\mu_{ji}\mu_{ri} \end{aligned} \quad (21)$$

The last term can be positive or negative. This gives rise to an interesting quantum interference effect: for a rotational level that is not in general that for which the perturbation lineshift is maximum (except when $|\mu_{ji}| = |\mu_{ri}|$) there is a complete extinction of the line and correlatively an enhancement of the other component: the quantum interference effect results in a complete transfer of intensity.

Let us now consider briefly bound-free perturbations, more precisely let us consider predissociation. In this case the bound B.O. level is quasi-degenerate with the dissociation continuum of another electronic state. This occurs for instance when the potential curve of the bound state is crossed by a dissociative potential curve or sometimes when a bound level lies higher than the dissociation continuum of another stable electronic state. When the two electronic states are coupled by some perturbation element H , the quasi-bound state contains in its wavefunction a more or less pronounced dissociative character. The net effect of this is to widen the corresponding lines in absorption as a consequence of the time-energy Heisenberg relation and to induce disappearance of the expected lines in emission.

Concerning the dynamics of the process, the effect of a predissociation is to add a non-radiative rate constant in the rate equation for the perturbed state:

$$dN/N = -(k_r + k_{nr})dt \quad (22)$$

which leads to:

$$N(t) = N_0 \exp[-(k_r + k_{nr})t] \quad (23)$$

The perturbed lifetime is given by:

$$1/\tau_{pert} = 1/\tau_r + 1/\tau_{nr} \quad (24)$$

with $1/\tau_{nr}$ deduced from the Fermi golden rule:

$$1/\tau_{nr} = 4\pi^2/h|He|^2 | \langle v | \chi_E \rangle |^2 \quad (25)$$

From this, the effect of predissociation is seen to decrease the lifetime of the perturbed state.

4 Methods

There are essentially three classes of methods that can be used to determine oscillator strengths in laboratory. Two of them are experimental methods and relate to absolute intensity measurements and to time-resolved spectroscopy, respectively. The third one consists in *ab initio* calculations of transition moments.

In the absolute intensity measurement method, the wavenumber-integrated absorption coefficient is computed from the equivalent width (Davis et al. 1986) deduced from the exponential (Beer-Lambert law) decrease in the incident flux over a path-length of absorbing gas. The difficulty arises in the passage from the macroscopic data to the microscopic ones. This requires to use the number density in the medium, an information that is in general poorly known for metal compounds that are difficultly volatile; indeed the uncertainty may sometimes turn on several orders of magnitude. Another way to proceed is to use, when possible, another known absolute transition probability of the same molecule as a mean for calibration. In spite of these difficulties the intensity method, when it can be worked out, is quite interesting because it yields directly individual level-to-level oscillator strengths.

The second method for determining oscillator strengths consists in attempting to extract them from lifetime measurements. The simplest method for measuring lifetimes is to compute them from the exponential decay of emission after fast removal of the pulsed dye-laser excitation. The advantage of this pulse-decay method is that it provides directly lifetimes without need for other data. Another way for probing the decay of the population of a state is to photoionize this state and to detect the decay of the number of ejected electrons (Doverstal & Weijnitz 1992). The experiments often involve a supersonic molecular beam, a device that displays the advantage of providing practically collision-free conditions. Another possibility offered by the molecular beam technique is to move

the measurement from time to space. Instead of the time constant of the decay one can measure the length over which molecules continue to emit after the excitation point and then divide by the mean velocity of the beam to convert this length into a lifetime. This method is especially suitable for long lifetimes since these correspond to significant lengths. Lifetime measurements can also be carried out in a simple cell at moderately high pressure (a few torrs). However it is then necessary to extrapolate the measured lifetimes to zero-pressure in order to eliminate the non-radiative part of the lifetime due to collisions. The lifetime measurement method has had a lot of variants. Among the most original ones, let us quote the recent lifetime measurements of Hikmet et al. (1992) on copper halide excited states up to high vibrational levels formed in reactive collisions of metastable copper atoms with halogen compounds. In this experiment the removal of excitation of the halide is obtained by stopping abruptly its formation in the excited state owing to a copper laser that depopulates instantaneously the metastable atomic copper state through stimulated emission.

In time-resolved spectroscopy the main problem is to prepare a sufficient concentration of excited molecules. This requires a powerful optical pumping device. The method is therefore restricted to the spectral regions where lasers operate (though other sources can be used in the UV such as synchrotron radiation [Castex et al. 1980]). Because of this, the time-resolved method is frequently called laser-induced decay measurements. Other complications may happen that alter the interpretation of the recorded results, for instance when multi-exponential decays occur due to intense transfers or cascading processes.

Though time-resolved spectroscopy is the ideal way for determining lifetimes, it is not able to yield values of individual state-to-state transition moments and oscillator strengths since it results in principle from depopulation over numerous vibronic channels. However, in a fairly large number of cases, it may happen that one particular electronic depopulation channel is favoured against all others. In such a case, the summation is restricted to the vibrational transitions within this single electronic channel. Owing to the closure condition on Franck-Condon factors, an approximate value of the electronic transition moment \mathcal{R}_e can then be obtained assuming that this moment is constant, and furthermore that all the $\nu_{v'v''}$ factors can be replaced by the ΔT_e electronic spectral term difference. One has then approximately:

$$(\tau_{v'})^{-1} \approx (16\pi^2/3h\epsilon_0)\mathcal{R}_e^2\Delta T_e^3 \quad (26)$$

Measuring experimentally $\tau_{v'}$ thus yields a rough value of \mathcal{R}_e^2 that can be multiplied by relevant Franck-Condon factors to go back to rough values of the $A_{v'v''}$ vibronic transition probabilities. Note, however, that this is nothing but a makeshift, though a useful one because lifetime measurements are often the only experimental way to have access to transition moments of metallic compounds, seeing the difficulty for doing quantitative absorption spectroscopy with them.

The last method, and in the author's opinion the most promising one, for obtaining oscillator strengths and lifetimes is to determine transition moments by means of ab initio calculations (see Langhoff & Bauschlicher, Malmqvist, and

Peyerimhoff, this volume). Some years ago such a statement would probably have been considered as somewhat arrogant. This is no longer so today. Recent state-of-the-art *ab initio* calculations have begun to reach such a level of sophistication that they are able to provide reliable determinations of oscillator strengths and lifetimes with an accuracy probably comparable to the experimental one, though it remains difficult to assess this accuracy *a priori* (Langhoff & Chong 1978).

The power of the *ab-initio* approach is threefold. First, it allows to determine the form of transition moments over any desired range of internal coordinates contrarily to experiment that can only sample a very limited geometry variation. Second, it applies to any transition, all the transitions of a molecule if wanted, even the least intense ones, whereas experiments either in emission or absorption suffer from severe limitations in the number of accessible transitions. Finally, it makes possible a fine understanding of the whole spectrum of a molecule, an identification of “dark” states that are important in dynamics studies, an interpretation of the relative role of orbitals, polarisation, and configuration interaction in the observed intensities. The force of *ab initio* calculations will be thoroughly illustrated below.

5 Radiative Properties: A Review of Data

The rest of this chapter is devoted to a review, molecule per molecule, of the present status of knowledge about oscillator strengths and lifetimes in the metallic monoxides and monohydrides. It is organized as follows. First the radiative properties of all the hydrides are reviewed following the order of the columns of the periodic classification, the transition and rare-earth series being put at the end. Then the same is done for monoxides.

5.1 Alkali Monohydrides: LiH, NaH, KH, CsH

Lithium monohydride LiH is the lightest molecule containing a metal. This gives it a special position that explains the attraction it has exerted on molecularists in spite of its little interest for astrophysicists even though this little interest probably arises out of certain practical circumstances, namely the fact that its electronic transitions lie far away in the ultraviolet.

Nevertheless the series of papers on LiH (Way & Stwalley 1973; Stwalley & Zemke 1976; Stwalley et al. 1977; Stwalley 1977; Zemke & Stwalley 1978, 1980; Zemke et al. 1978; Vidal & Stwalley 1982, 1984) published between 1973 and 1984 represents a fine example of the application of the ideas developed above. These authors decided to calculate systematically radiative transition probabilities for the three systems interconnecting the $X^1\Sigma^+$, $A^1\Sigma^+$ and $B^1\Pi$ states of LiH. The electronic transition moments $\mathcal{R}_e(R)$ had already been carefully calculated by Docken & Hinze (1972) and these *ab initio* data were used by Zemke et al. with minor extrapolations. It should be noted that a recent re-calculation of these moments (Gadea 1993) has confirmed the accuracy of Docken's and Hinze's work. Then Zemke et al. constructed full potential curves for the three

states using spectroscopic data (see Huber & Herzberg 1979) from which they deduced all the bound vibrational energy levels as well as their wavefunctions. Combining the *ab initio* data and the experimental potential curves they calculated oscillator strengths and transition probabilities between all bound vibronic levels. They also calculated lifetimes of each v' level by summing the $A_{v',v''}$ Einstein coefficients over all the lower-lying vibrational levels v'' including bound levels and also (less accurately) free levels from the dissociation continuum of the ground state. Thus in the A state the bound-free contribution to the lifetime, completely negligible at low v' , was found to become predominant for levels above $v'=17$. Zemke et al. also estimated the magnitude of the predissociation of the A vibronic levels by the $X^1\Sigma^+$ dissociation continuum and found that it was completely negligible in LiH. The results obtained by Zemke et al. are in excellent agreement with the experimental determinations of lifetimes by Dagdigian (1976), Wine & Melton (1976), Brieger et al. (1983) for the $A^1\Sigma^+$ state and by Von Moers et al. (1987) for the $B^1\Pi$ state.

For NaH, there are also both theoretical and experimental results. Sachs et al. (1975) have carried out *ab initio* calculations of electronic transition moments similar to those of Docken & Hinze (1972) on LiH but extended to some triplet-triplet transitions in addition to the singlet-singlet ones. They predicted band oscillator strengths and Einstein coefficients for the most intense system, the $A^1\Sigma^+-X^1\Sigma^+$ one. Their calculation was later used by Telle (1986) to predict lifetimes of the $A^1\Sigma^+$ vibronic levels of NaH. These semi-theoretical results fit well with the experimental measurements carried out by Baltayan et al. (1976) for $v' = 3-5$, by Dagdigian (1976) for $v'=8$, by Brieger et al. (1981, 1983) for $v' = 12-15$, and still higher by Nedelec & Giroud (1983) except for the anomalously long lifetime found for the highest level reached in this last study ($v'=21$) that was attributed to potential curve crossing at long internuclear distance.

Very few results exist for KH. Its fluorescence was observed by dye-laser excitation by Cruse & Zare (1974), Ihle & Wu (1974), and Ennen & Ottinger (1975), but with so high a pressure that relaxation was more rapid than the laser pulse decay. Using a heat-pipe oven, Giroud & Nedelec (1982) were able to measure the lifetime of the $A^1\Sigma^+$ state of KH. For the highest vibrational level they pointed out a sudden decrease of the lifetime at the opposite of their finding for NaH (Nedelec & Giroud 1983).

Such a sudden decrease of the lifetime appears also in CsH and this even in fairly low vibrational levels of the $A^1\Sigma^+$ state (as low as $v'=12$). This was clearly reported by Ferray et al. (1984) after the first measurements by Tam & Happer (1976) and Hsie et al. (1978) on this molecule. In fact the measured lifetime falls at an approximately constant value that is just equal to the lifetime of the cesium atomic state corresponding to the dissociation. This strongly suggests that this effect is due to predissociation of the highest vibrational levels of CsH ($A^1\Sigma^+$) by the continuum of the ground state. This effect, unobserved in the light LiH and NaH hydrides and suspected at the highest v' in KH, becomes quite clear in CsH. It has been reproduced theoretically by Telle (1984, 1986), though considerably smoothed over, on the basis of the *ab initio* transition moment calculations of

Laskowski & Stallcop (1981). It would be interesting to measure the lifetimes in RbH to see whether the same predissociation effect is present or not in this heaviest alkali hydride for which no lifetime measurement has yet been reported.

5.2 Alkaline-earth Hydrides: MgH, CaH

MgH has considerable astrophysical importance. Transition probabilities have been calculated by Henneker & Popkie (1971) and Popkie (1971). These *ab initio* predictions, though less refined than what can be done nowadays, are in good agreement with the values of lifetimes determined later by Nedelec & Dufayard (1978) for the $v'=0$ and $v'=1$ levels of the $A^2\Pi$ states of MgH and MgD (between 40 and 50 ns).

For CaH, Klynning et al. (1982) determined the perturbation-free lifetimes of the $B^2\Sigma^+$ ($v=0$) state to be 57 ns leading to an absorption oscillator strength equal to 0.11.

5.3 Boron and Aluminium Hydrides: BH, AlH

Laboratory measurements of the lifetime of the lowest vibronic level of the $A^1\Pi$ state ($\tau=125\pm 5$ ns) of BH have been reported by Dufayard & Nedelec (1978). Calculations by Douglas et al. (1989) reproduce fairly well the only experimentally reported lifetimes, thus giving confidence in the other calculated quantities.

Similar experiments using laser-induced fluorescence for the corresponding $A^1\Pi$ states of AlH and AlD have also been carried out for the $v'=0$ and $v'=1$ levels by Baltayan & Nedelec (1979). The lifetime values they found were noticeably shorter than in BH ($\tau_0=66$ ns and $\tau_1=83$ ns in AlH). An interesting result in AlH is their measurements of the lifetimes of rotational levels in the $v'=1$ state in the region of the predissociation: the first predissociated rotational level, $N'=6$, has a much shorter lifetime (50 ns) than the preceding level, $N'=5$, (83 ns), that does not suffer significantly from this predissociation.

Three *ab initio* calculations have been published relating to potentials and transition moments for the A state of AlH. These were obtained from full-CI calculations by Bauschlicher & Langhoff (1988), from CASSCF calculations by Matos et al. (1987) and by the polarization propagator method by Scuseria et al. (1989). Here also, the agreement with experimental lifetimes is reasonably good and even less sensitive to the shape of the potential curves than in BH. However a good agreement for lifetimes does not definitely ascertain the reliability of the level-to-level quantities that enter in this global value. Thus, Rice et al. (1992) recently determined ratios of the Einstein coefficients and band oscillator strengths involving five bands of the $A^1\Pi-X^1\Sigma^+$ transition of AlH by using relative integrated intensities. Owing to a calibration based on Baltayan's and Nedelec's lifetimes (1979), they derived absolute Einstein coefficients. They found that the so-measured values of these coefficients were considerably smaller than the calculated ones (Matos et al. 1987) whereas the overall summation carried out by these authors to obtain theoretical values of lifetimes were in much

better agreement with experiment, probably because of compensating balance effects to be associated with the closure relation on Franck-Condon factors.

5.4 Group IV-A Metallic Hydrides: GeH, SnH, PbH

Only the heavy members of the Group IV-A of the periodic table will be considered here since the others, carbon and silicon, are metalloids and do not enter into the scope of this review.

Three experimental lifetime determinations have been published for GeH. All of them relate to the lowest excited doublet state $A^2\Delta$. Osmundsen et al. (1985) report a rather short lifetime of 12 ± 2 ns for the three lowest vibrational levels in the photolysis of GeH_4 . The largest and agreeing values of about 80 ± 5 ns determined by Erman et al. (1989) and of 93 ± 10 ns found in laser-induced fluorescence by Bauer et al. (1989) for the $A^2\Delta$ ($v'=0$) level seem to be more reliable. These values are about six times smaller than in CH (Bauer et al. 1989). This is explained by the predissociation of the GeH $A^2\Delta$ state (Erman et al. 1989). It would be interesting to determine the τ_{nr} part of this predissociation in the total lifetime by a simple difference between the experimental transition probability and that deduced from the ab initio transition moment calculations performed by Chapman et al. (1988).

For the SnH and PbH molecules, the first and up to now the only known moments come from theoretical calculations, not experiment as is generally the case. Like for GeH, Chapman et al. (1988) determined the transition moments of the $^2\Delta - ^2\Pi$ and $^4\Sigma^- - ^2\Pi$ systems from refined ab initio calculations using a $\omega - \omega$ coupling scheme. In principle, oscillator strengths could be calculated from these data, but the predissociation could probably not be ignored in this case as it could strongly affect the pure radiative values.

5.5 Transition Element Hydrides: ScH, TiH, FeH, MnH, ZnH, CdH, HgH

Transition elements are known to be present in circumstellar atmospheres. Although dissociation equilibrium simulations by Querci (1993) seem to indicate that their hydrides are in general less abundant than the corresponding oxides, their astrophysical importance cannot be denied. Molecules like FeH and TiH for instance have been clearly identified in stellar sources (Wing et al. 1977; Yerle 1979) and NiH, CrH and MnH among others are strongly expected to be present in non-negligible amount. However the structure of their spectra are often not yet fully understood and there has been only a few attempts to measure oscillator strengths and lifetimes for some of these compounds. Most of the information about their dynamics comes from recent careful ab initio calculations.

Thus for ScH and TiH, Anglada et al. (1989, 1990) systematically computed a large number of transition moments starting from several low-lying states. These calculations were meant to identify the most intense transitions. As they were done at a single separation, the R-dependence of the moments is not known and

oscillator strengths and lifetimes cannot be deduced from them with accuracy. Anglada et al. (1990) also quote unpublished calculations on VH and YH.

The transition moments of FeH have been calculated by Langhoff & Bauschlicher (1990) who use them to compute Einstein coefficients for the strong $F^6\Delta-X^6\Delta$ band system. They also calculate lifetimes for several states: $e^6\Pi$ (53ns), $g^6\Phi$ (55ns), $F^6\Delta$ (1 μ s), $A^4\Pi$ (4 μ s) and some electronic oscillator strengths.

Similar calculations on MnH by Langhoff et al. (1989) provide a number of ab initio transition moment functions for the quintet and septet states. From these it has been possible to compute Einstein coefficients for the three strongest transitions of MnH and to derive radiative lifetimes for the four lowest vibronic levels of the $A^7\Pi$ ($\tau=0.1\mu$ s), $b^5\Pi$ ($\tau=2-3\mu$ s) and $c^5\Sigma^+$ ($\tau=0.3\mu$ s) states.

The only experimental data about radiative effects in transition metal hydrides are the lifetime measurements of Jourdan et al. (1976) on CdH and CdD, those of Dufayard & Nedelec (1977) on ZnH, ZnD, CdH and CdD and those of Nedelec & Dufayard (1978) on HgH and HgD, relating to the $A^2\Pi$ state. These authors report a lifetime of about 70 ns for the $v'=0$ and $v'=1$ levels of the A states of the zinc and cadmium hydrides and a little longer for HgH (101ns) and HgD (134ns).

5.6 Alkali Oxides: LiO, NaO, KO

The observed electronic spectrum of alkali monoxides is limited to a spread progression of vibronic bands that have been found in the red and the near infrared (Woodward et al. 1989; Pfeifer & Gole 1984). The multiple collision conditions necessary for its observation are not favourable to experimental dynamic measurements. This explains why the only paper about the lifetimes of LiO, NaO, and KO is an ab initio one due to Langhoff et al. (1992). These authors have calculated the radiative lifetimes for the $C^2\Pi$ ($v'=0$) level to be 66, 91 and 315 ns for LiO, NaO and KO, respectively. They have shown that the depopulation channel towards the $X^2\Pi$ ground state is the only significant one. Nothing is known about CsO and RbO spectroscopy.

5.7 Alkaline-earth Monoxides: BeO, MgO, CaO, SrO, BaO

A great deal of literature has been devoted to alkaline-earth monoxide spectroscopy. For BeO, however, no experimental data about lifetimes and oscillator strengths seem to have been published. To our knowledge, the only available information about transition moments in BeO is the full configuration interaction benchmark calculations by Bauschlicher & Langhoff (1988) for selected dipole and quadrupole transitions.

There are many more results for MgO. Here also, several ab initio calculations have been published. The first one dates back to 1974. Huron et al. (1974) performed configuration interaction calculations of ten transition dipole moments in the singlet and in the triplet manifolds. They were led to criticize a previous experimental determination of the $B^1\Sigma^+-X^1\Sigma^+$ oscillator strength by Main et

al. (1967; 1969). The discrepancy between experiment and theory for this system and others was kept going by the shock-tube quantitative absorption data of Evans & Mackie (1977) and of Svyatkin et al. (1980a) that both involved however perilous number density determinations. A better agreement was obtained for lifetime measurements from fluorescence decay. Thus the lifetime for the $v=0$ level of the $B^1\Sigma^+$ state that depopulates via two electronic channels towards $A^1\Pi$ and $X^1\Sigma^+$ was experimentally measured to be 21.5 ns by Busener et al. (1987) or 32.7 ns by Diffenderfer et al. (1983) who also derived a theoretical value of 24 ns. In the same way, there is good agreement between the experimental value (11.8 ns) reported for the lifetime of the $d^3\Delta$ state (Diffenderfer et al. 1983) and the theoretical one (9.3 ns) calculated by Yarkony (1988).

All the data for the heavier alkaline-earth oxides are of experimental nature. For CaO, Svyatkin et al. (1980 b,c) determined the $B^1\Pi-X^1\Sigma^+$ and $C^1\Sigma^+-X^1\Sigma^+$ electronic transition strengths using the same shock-tube absorption intensity measurements as in their work on MgO (Svyatkin et al. 1980a). Pasternack & Dagdigian (1978) estimated the overall lifetime of the upper states that produce the orange arc bands to be 32.7 ns and Irvin & Dagdigian (1981) found a lifetime of 155 ± 60 ns for the $v=6$ level of the $A^1\Sigma^+$ state. These lifetime values have been recently confirmed with better accuracy (27.8 ± 1.2 and 149 ± 11 ns, respectively) by Plane & Nien (1991).

For SrO, the only information on the transition probabilities are the works of Svyatkin et al. (1982) that studied the absorption intensities of the B-X and C-X transitions as a continuation of their series on alkaline-earth oxides and of Belyaev et al. (1982) who determined the transition probability of the B-X system from flame absorption spectrometry.

Only laser-induced fluorescence has been used to study BaO. The vibronic lifetimes of several states were determined. Thus Johnson (1972) measured average lifetimes of levels of the $A^1\Sigma^+$ state and found values around $0.35\mu\text{s}$. Three years later Pruett & Zare (1975) measured the lifetime of the $A'^1\Pi$ state to be $9\mu\text{s}$. They turned to account the difference between the A and A' lifetimes to separate the weak, long-lifetime A'-X fluorescence by delaying the observation of the A'-X emission until the A-X emission dies away. Hsu et al. (1980) investigated the relaxation of the $C^1\Sigma^+$ state in its three lowest vibrational levels, finding a short lifetime of 10 ns. From relative intensity measurements, they were able to measure fluorescence branching ratios and to show that the value obtained for this lifetime was the result of not less than four competing depopulation electronic channels for which they determined electronic dipole transition moments. Finally, Darrah & Silvers (1985), going back to the $A^1\Sigma^+$ state, studied the effects of perturbations on the rotational level lifetimes and observed lifetime lengthenings by a factor of two within a single vibronic state because of perturbation by components of the metastable $b^3\Pi$ state.

5.8 Boron and Aluminium Oxides: BO_2 , BO, AlO

Using a pulsed dye laser, Huie et al. (1978) observed the fluorescence of boron dioxide BO_2 and measured lifetimes of vibrational levels of the $A^2\Pi_u$ state. They

report $\tau(000)=87.2\pm 2.6$ ns and $\tau(100)=76.3\pm 1.4$ ns for this triatomic molecule which appears as being the only one involving a metal for which radiative data have been published.

In the same paper, Huie et al. (1978) also determined radiative lifetime values for the $v'=1$ and $v'=2$ levels of the $A^2\Pi$ state of boron monoxide BO. They found $\tau_1=131\pm 15$ ns and $\tau_2=103\pm 6$ ns, respectively. Two years later, Clyne & Heaven (1980) reported much longer lifetimes for the $v'=0$ ($\tau_0=1780\pm 40$ ns) and the $v'=4$ ($\tau_4=1940\pm 170$ ns) of this $A^2\Pi$ state. Configuration interaction calculations of the transition probabilities by Kozlov et al. (1990) seem to be in favour of the short lifetimes given by Huie (1978) though their results depend strongly on the molecular orbital basis used in their computations.

For AlO the determination of the $B^2\Sigma^+ - X^2\Sigma^+$ oscillator strengths and of the lifetime of the $B^2\Sigma^+$ state is full of controversy. Here again absolute intensity measurements are difficult because they are subject to large systematic uncertainties in the determination of the molecular concentration. The oscillator strengths determined by this method by Vanpee et al. (1970) from flame emission and by Hooker & Main (1971) from shock-tube absorption are an order of magnitude shorter than the most recent values deduced from laser fluorescence. Other emission intensity measurements by Hebert & Tyte (1964) and by Tyte & Hebert (1964) as well as shock-tube studies by Linton & Nicholls (1969) were re-calibrated by Hebert et al. (1980) using independently determined lifetimes (Johnson et al. 1972; Dagdigian et al. 1975); thus the concentration measurement problem was avoided and more reliable values could be obtained. Fluorescence decay measurements proved again to be the best method in this case. Of the five $B^2\Sigma^+$ lifetime determinations using this method, four give comparable results. These are the measurements by Johnson et al. (1972): $\tau_0=128\pm 6$ ns; by Dagdigian et al. (1975): $\tau_0=100\pm 7$ ns, $\tau_1=102\pm 7$ ns; by Salzberg et al. (1991): $\tau_1=97\pm 12$ ns, and by Campbell et al. (1992): $\tau_1=102\pm 10$ ns. It seems that the value of $\tau_0=272\pm 14$ ns reported by Wentink et al. (1971) in the fifth paper, the oldest one, should be rejected. It would be interesting to compare these results to a careful *ab initio* determination. The two theoretical studies due to Michels (1972) and to Yoshimine et al. (1973) date back to the early seventies and could be much refined today.

5.9 Transition Metal and Rare-earth Oxides: ScO, YO, TiO, ZrO, FeO, CuO, LaO

Unlike the case of the hydrides, the literature on radiative properties of the transition element oxides is mainly of experimental rather than of theoretical nature. This is due to the large number of electrons to correlate, which makes *ab initio* calculations somewhat more difficult on oxides than on hydrides, especially for such sensitive quantities as transition moments.

In the course of their study of nascent product state distributions in reactions of Group III-B atoms with various oxidizers, Liu & Parson (1977) detected time-resolved fluorescence from which they deduced the lifetimes of molecular excited states in various vibronic levels. These measurements concern the first excited

${}^2\Pi$ and ${}^2\Sigma^+$ electronic states of ScO, YO and LaO. All the measured lifetimes lie in the range 25–40 ns. These values compare well with those measured in the isoelectronic alkaline-earth monohalides by Dagdigan et al. (1974).

For LaO, recent measurements using laser-induced decay fluorescence have been carried out by Carette & Bencheik (1993). This study confirms the lifetime found by Liu & Parson (1977) for the $B^2\Sigma^+$ state (32 ns instead of 34 ns) but not for the $C^2\Pi$ state for which they find a three-times longer lifetime (77 ns instead of 27 ns).

There has been considerable interest in the determination of radiative properties of titanium monoxide TiO that is known to be one of the main features in the absorption spectra of M-type stars (Kieess 1948; Merrill et al. 1962; Machara & Yamashita 1976). The time-resolved laser/pulse-fluorescence decay method has been widely used for TiO. It led to the determination of lifetimes around 30 ns for the $v'=0,1,2$ vibrational levels of the $C^3\Delta$ state (Steele & Linton 1978). Feinberg & Davis (1976, 1977) also measured a short lifetime of 17.5 ns for the $c^1\Phi$ state. Recently, the same method was used by Simard & Hackett (1991) for the long lifetime of the $E^3\Pi$ ($v=0$) state (770 ± 40 ns), by Doverstal & Weijnitz (1992) for the $v=0$ levels of the $A^3\Phi_2$ ($\tau=102$ ns), $B^3\Pi_0$ ($\tau=55$ ns) and $C^3\Delta_1$ ($\tau=32$ ns) states and by Carette & Schamps (1992) for the $B^3\Pi$ ($v=1$) state ($\tau=44\pm 2$ ns). This last value is in excellent agreement with that determined by Davis et al. (1986) from absorption coefficient measurements that concerned also $A^3\Phi$ ($\tau=51\pm 9$ ns, i.e. half the recent value found from population probing techniques by Doverstal & Weijnitz [1992]), $C^3\Delta$ ($\tau=18.5\pm 3$ ns, smaller than values from time-resolved spectroscopy) and $b^1\Pi$ ($\tau=192\pm 55$ ns, the only experimental determination for this state). Various other determinations of oscillator strengths (leading to lifetime values assuming a single-channel depopulation) have been performed by absorption-coefficient measurements (Golden 1967; Collins & Faÿ 1974) or absolute-intensity studies (Zyrnicki 1975; Price et al. 1971, 1974; Linton & Nicholls 1970). Recently, ab initio calculations for TiO were carried out by Schamps et al. (1992) that reproduced well the lifetimes of short-lived states. This agreement enabled them to predict a value of 42 ns for the as yet unmeasured lifetime of the $f^1\Delta$ state. However, the agreement for the long-lived $E^3\Pi$ and $b^1\Pi$ states was much less satisfactory by factors of more than two as a probable consequence of an insufficient description of electronic correlation in their calculations.

The other transition-element monoxides are much less documented. For ZrO, that is isovalent to TiO, only the lifetime of the $J'=17$, $v'=0$ level of the $B^3\Pi$ state has been measured (Hammer & Davis 1979). The analysis of the decay of resonant fluorescence radiation led to a value of 32.5 ± 2 ns for the lifetime of the B state from which transition probabilities and oscillator strengths for the bands of the $B^3\Pi-X^3\Delta$ system were estimated. Fortunately the theoretical study of the spectroscopy of the ZrO molecule by Langhoff & Bauschlicher (1990) counterbalances the lack of experimental data.

FeO was studied by West & Broida (1975) whose photoluminescence and chemiluminescence experiments allowed to determine lifetimes of the order of

450±100 ns for the radiative lifetimes of the $A^5\Sigma^+$ and $B^5\Pi$ upper electronic states of the orange bands.

Finally, two studies should be mentioned for CuO. The first one concerns the pulse-decay determination of lifetimes of four ionic valence states: $A^2\Sigma^-$ ($\tau=0.65 \mu\text{s}$), $C^2\Pi$ ($\tau=1.3 \mu\text{s}$), $D^2\Delta$ ($\tau=1.8 \mu\text{s}$), $A'^2\Sigma^+$ ($\tau > 5 \mu\text{s}$). This study made possible a separation of quartet states from doublet ones on the basis of large differences in their lifetime magnitudes (Delaval et al. 1983). The second study is an ab initio calculation on the spectroscopy of CuO (Hoppe & Peyerimhoff 1992). In this study transition moments and lifetimes were systematically computed for numerous valence states in various molecular orbital bases. In spite of the strong dependence of results on the basis used, correspondence between observed and calculated states could be given although the situation is quite complicated in this molecule.

6 Conclusion

The transition element and lanthanide oxide data complete this review that the author wishes to be as exhaustive as possible. Some papers have probably escaped his bibliographic search and he will be grateful to those readers who will be kind enough to mention to him any omission or mistake he could have made.

The major conclusion that arises from this compilation is the urgent need for further experiments and calculations on radiative properties of small molecules. In spite of the abundant literature on the subject, the number of molecules, and for each of these molecules the number of band systems, that have been sampled from the point of view of radiative dynamics is eventually scarce compared to what remains to do. It would be much longer to list all the molecules, if only diatomics, for which radiative properties have not been investigated at all than those for which something is known. For astrophysicists the priority should concern those poorly studied molecules that are yet expected to be significantly present in cool stellar sources, e.g. FeO, LaO, ScO, VO, YO, NiO, CoO, AlO, CaO, NiO₂, YO₂, ScO₂, ZrO₂, VO₂, and the corresponding hydrides.

Yet the situation evolves in the right direction. Whereas the possibilities for getting new experimental data seem to slow down, if not to saturate, the fast development of ab initio calculations is more than encouraging. Computer facilities and program improvements have significantly increased the possibilities of quantum chemistry. Electronic transition moments can now be computed with an accuracy that rivals the best experimental determinations. Even they replace them in the extremely frequent cases when experimental measurements are not feasible. However, one must be cautious about the use of ab initio calculations in predicting accurate radiative properties. For example, small shifts in potential curves may sometimes change drastically the calculated values of oscillator strengths. Also, the possible presence of predissociation effects may decrease, by orders of magnitude, the radiative lifetimes deduced from only the calculated transition moments. Anyway, in the vast majority of cases, ab initio calculations, checked whenever possible by experimental measurements, should be the

key for providing a dramatic increase in our knowledge about molecular radiative properties in the coming years.

References

- Anglada J., Bruna P.J., Peyerimhoff S.D., 1989, *Molec. Phys.*, **66**, 541
Anglada J., Bruna P.J., Peyerimhoff S.D., 1990, *Molec. Phys.*, **69**, 281
Baltayan P., Jourdan A., Nedelec O., 1976, *Phys. Letters*, **58A**, 443
Baltayan P., Nedelec O., 1979, *J. Chem. Phys.*, **70**, 2399
Bauer W., Engelhardt B., Wiesen P., Becker H., 1989, *Chem. Phys. Letters*, **158**, 321
Bauschlicher C.W., Langhoff S.R., 1988, *J. Chem. Phys.*, **89**, 2116
Bauschlicher C.W., Langhoff S.R., 1988, *Theor. Chem. Acta*, **73**, 43
Belyaev V.N., Lebedeva N.L., Krasnov K.S., Gurvich L.V., 1982, *Opt. Spectrosc.*, **55**, 1075
Born M., Oppenheimer R., 1927, *Ann. Physik*, **84**, 457
Brieger M., Hese A., Penn A., Sodeik A., 1981, *European Conf. on Atomic Physics*, Heidelberg, p.353
Brieger M., Penn A., Sodeik A., Hese A., 1983, *Chem. Phys.*, **75**, 1
Busener H., Heinrich F., Hese A., 1987, *Chem. Phys.*, **112**, 139
Campbell M.L., McClean R.E., Garland N.L., Nelson H.H., 1992, *Chem. Phys. Letters*, **194**, 187
Carette P., Schamps J., 1992, *J. Molec. Spectrosc.*, **154**, 448
Carette P., Bencheikh M., 1993, to be published
Castex M.C., LeCalve J., Haaks D., Jordan B., Zimmerer G., 1980, *Chem. Phys. Letters*, **70**, 106
Chapman D.A., Li J., Balasubramanian K., Lin S.H., 1988, *J. Chem. Phys.*, **88**, 3826
Clyne M.A., Heaven M.C., 1980, *Chem. Phys.*, **51**, 299
Collins J.G., Faÿ T.D., 1974, *J. Quant. Spectrosc. Radiat. Transfer*, **14**, 1259
Cruse J.A., Zare R.N., 1974, *J. Chem. Phys.*, **60**, 1182
Dagdigian P.J., Cruse J.A., Zare R.N., 1974, *J. Chem. Phys.*, **60**, 2330
Dagdigian P.J., Cruse J.A., Zare R.N., 1975, *J. Chem. Phys.*, **62**, 1824
Dagdigian P.J., 1976, *J. Chem. Phys.*, **64**, 2609
Darrah S.D., Silvers S.J., 1985, *Chem. Phys. Letters*, **121**, 377
Davis S.P., Littleton J.E., Phillips J.G., 1986, *Astrophys. J.*, **309**, 449
Delaval J.M., David F., Lefebvre Y., Bernage P., Niay P., Schamps J., 1983, *J. Molec. Spectrosc.*, **101**, 358
Diffenderfer R.N., Yarkony D.R., Dagdigian P.J., 1983, *J. Quant. Spectrosc. Radiat. Transfer*, **29**, 329
Docken K.K., Hinze J., 1972, *J. Chem. Phys.*, **57**, 4928
Docken K.K., Hinze J., 1972, *J. Chem. Phys.*, **57**, 4936
Douglas C.H., Nelson H.H., Rice K.J., 1989, *J. Chem. Phys.*, **90**, 6940
Doverstal M., Lindgren B., Sassenberg U., Yu H., 1991, *Physica Scripta*, **42**, 572
Doverstal M., Weijnitz P., 1992, *Molec. Phys.*, **75**, 1357
Dufayard J., Nedelec O., 1977, *J. Phys.*, **38**, 449
Dufayard J., Nedelec O., 1978, *J. Chem. Phys.*, **69**, 4708
Ennen G., Ottinger C., 1975, *Chem. Phys. Letters*, **36**, 16
Erman P., Gustavsson O., Larsson M., 1983, *Physica Scripta*, **27**, 256
Evans P.J., Mackie J.C., 1977, *J. Molec. Spectrosc.*, **65**, 169
Feinberg J., Bilal M.G., Davis S.P., Phillips J.G., 1976, *Appl. Letters*, **17**, 147

- Feinberg J., Davis S.P., 1977, *J. Molec. Spectrosc.*, **65**, 264
- Feinberg J., Davis S.P., 1978, *J. Molec. Spectrosc.*, **69**, 445
- Ferray M., Visticot J.P., Sayer B., Telle H.H., 1984, *J. Chem. Phys.*, **81**, 191
- Gadea X., 1993, to be published
- Giroud M., Nedelec O., 1982, *J. Chem. Phys.*, **77**, 3998
- Golden S.A., 1967, *J. Quant. Spectrosc. Radiat. Transfer*, **7**, 225
- Hammer P.D., Davis S.P., 1979, *J. Molec. Spectrosc.*, **78**, 337
- Hebert G.R., Tyte D.C., 1964, *Proc. Phys. Soc.*, **83**, 629
- Hebert G.R., Nicholls R.W., Linton C., 1980, *J. Quant. Spectrosc. Radiat. Transfer*, **23**, 229
- Henneker W.H., Popkie H.E., 1971, *J. Chem. Phys.*, **54**, 1763
- Herzberg G.H., 1950, *Spectra of Diatomic Molecules*, Van Nostrand, N.Y.
- Hikmet I., Kowalczyk P., Sadeghi N., 1992, *Chem. Phys. Letters*, **188**, 287
- Hippe D., Peyerimhoff S.D., 1992, *Molec. Phys.*, **76**, 293
- Hooker W.J., Main R.P., 1971, *AI(O(A-X)oscillator strengths and collisional relaxation rates*, Final Rep., KMS Techn. Center, Glendale, Cal.
- Hsieh Y.K., Yang S.C., Tam A.C., Stwalley W.C., 1978, *J. Chem. Phys.*, **68**, 1448
- Hsu Y.C., Hegemann B., Pruett J.G., 1972, *J. Chem. Phys.*, **72**, 6437
- Huber K.P., Herzberg G.H., 1979, *Constants of Diatomic Molecules*, Van Nostrand, N.Y.
- Huie R.E., Long N.J.T., Thrush B.A., 1978, *Chem. Phys. Letters*, **55**, 404
- Huron B., Malrieu J.P., Rancurel P., 1974, *Chem. Phys.*, **3**, 277
- Ihle H.R., Wu G.H., 1974, *J. Chem. Phys.*, **63**, 1605
- Irvin J.A., Dagdigian P.J., 1981, *J. Chem. Phys.*, **74**, 6178
- Johnson S.E., 1972, *J. Chem. Phys.*, **56**, 149
- Johnson S.E., Capelle G., Broida H.P., 1972, *J. Chem. Phys.*, **56**, 663
- Jourdan A., Negre J.M., Dufayard J., Nedelec O., 1976, *J. Phys. Lettres*, **37**, L29
- Kiess C.C., 1948, *Publ. Astr. Soc. Pacif.*, **60**, 252
- Klynning L., Martin H., Nylen P., Royen P., 1982, *Physica Scripta*, **25**, 362
- Kovacs I., 1969, *Rotational Structure in the Spectra of Diatomic Molecules*, Hilger, London
- Kozlov V.A., Pupyshev V.I., Stepanov N.F., 1990, *Opt. Spectrosc.*, **68**, 595
- Kuzmenko N.E., Kuznetsova L.A., Monyakin A.P., Kuzyakov Y.Y., Plastinin Y.A., 1979, *Sov. Phys. Usp.*, **17**, 405
- Kuznetsova L.A., Kuzmenko N.E., Kuzyakov Y.Y., Plastinin Y.A., 1980, *Optical Probabilities in Diatomic Molecules*, Nauka, Moscow
- Langhoff S.R., Chong D.P., 1978, *J. Chem. Phys.*, **69**, 194
- Langhoff S.R., Bauschlicher C.W., Rendell A.P., 1989, *J. Molec. Spectrosc.*, **138**, 108
- Langhoff S.R., Bauschlicher C.W., 1990, *J. Molec. Spectrosc.*, **141**, 243
- Langhoff S.R., Bauschlicher C.W., 1990, *Astrophys. J.*, **349**, 369
- Langhoff S.R., Partridge H., Bauschlicher C.W., 1992, *Chem. Phys.*, **153**, 1
- Larsson M., 1983, *Astron. Astroph.*, **128**, 291
- Laskowski B., Stallcop J.R., 1981, *J. Chem. Phys.*, **74**, 4883
- Lefebvre-Brion H., Field R.W., 1986, *Perturbations in the Spectra of Diatomic Molecules*, Academic Press, N.Y.
- Linton C., Nicholls R.W., 1969, *J. Quant. Spectrosc. Radiat. Transfer*, **9**, 1
- Linton C., Nicholls R.W., 1970, *J. Quant. Spectrosc. Radiat. Transfer*, **10**, 311
- Liu K., Parson J.M., 1977, *J. Chem. Phys.*, **67**, 1814
- Machara H., Yamashita Y., 1976, *Publ. Astr. Soc. Japan*, **28**, 135

- Main R.P., Carlson D.J., Dupuis R.A., 1967, *J. Quant. Spectrosc. Radiat. Transfer*, **7**, 805
- Main R.P., Schadee A., 1969, *J. Quant. Spectrosc. Radiat. Transfer*, **9**, 713
- Matos J.M.O., Malmqvist P.A., Roos B.O., 1987, *J. Chem. Phys.*, **86**, 5032
- Merril P.J., Deutsch A.J., Keenan P.C., 1962, *Astrophys. J.*, **136**, 121
- Michels H.H., 1972, *J. Chem. Phys.*, **56**, 665
- Nedelec O., Dufayard J., 1978, *J. Chem. Phys.*, **69**, 1833
- Nedelec O., Giroud M., 1983, *J. Chem. Phys.*, **79**, 2121
- Nicholls R.W., Stewart A.L., 1962, in *Atomic and Molecular Processes*, ed.D.R.Bates, Academic Press, N.Y.
- Nicholls R.W., 1969, in *Physical Chemistry-III*, ed.H.Eyring,D.Henderson&W.Yost, Academic Press, N.Y.
- Osmundsen J.F., Abele C.C., Eden J.G., 1985, *J. Chem. Phys.*, **83**, 2159
- Pasternack L., Dagdigian P.J., 1978, *Chem. Phys.*, **33**, 1
- Pfeifer J., Gole J.L., 1984, *J. Chem. Phys.*, **80**, 565
- Plane J.M., Nien C.F., 1991, *J. Chem. Soc. Faraday Trans.*, **87**, 677
- Popkie H.E., 1971, *J. Chem. Phys.*, **54**, 4597
- Price M.L., Sulzmann K.G., Penner S.S., 1971, *J. Quant. Spectrosc. Radiat. Transfer*, **11**, 427
- Price M.L., Sulzmann K.G., Penner S.S., 1974, *J. Quant. Spectrosc. Radiat. Transfer*, **14**, 1273
- Pruett J.G., Zare R.N., 1975, *J. Chem. Phys.*, **62**, 2050
- Querci F., 1993, unpublished
- Rice J.K., Pasternack L., Nelson H.H., 1992, *Chem. Phys. Letters*, **189**, 43
- Russell H.N., 1934, *Astrophys. J.*, **79**, 317
- Salzberg A.P., Santiago D.I., Asmar F., Sandoval D.N., Weiner B.R., 1991, *Chem. Phys. Letters*, **180**, 161
- Sachs E.S., Hinze J., Sabelli N.H., 1975, *J. Chem. Phys.*, **62**, 3384
- Schadee A., 1967, *J. Quant. Spectrosc. Radiat. Transfer*, **7**, 169
- Schadee A., 1971, *Astron. Astrophys.*, **14**, 401
- Schadee A., 1978, *J. Quant. Spectrosc. Radiat. Transfer*, **19**, 451
- Schamps J., Sennesal J.M., Carette P., 1992, *J. Quant. Spectrosc. Radiat. Transfer*, **48**, 147
- Scuseria G.E., Geertsen J., Oddershede J., 1989, *J. Chem. Phys.*, **90**, 2338
- Simard B., Hackett P.A., 1991, *J. Molec. Spectrosc.*, **148**, 127
- Steele R.E., Linton C., 1978, *J. Molec.Spectrosc.*, **69**, 66
- Stwalley W.C., Zemke W.T., 1976, *Int. J. Quantum Chem. Symp.*, **10**, 223
- Stwalley W.C., Zemke W.T., Way K.R., Li K.C., Proctor R., 1977, *J. Chem. Phys.*, **66**, 5412
- Stwalley W.C., Zemke W.T., Way K.R., Li K.C., Proctor R., 1977, *J. Chem. Phys.*, **67**, 4785
- Stwalley W.C., 1977, *Contemp. Phys.*, **18**, 65
- Svyatkin I.A., Kuznetsova L.A., Kuzyakov Y.Y., Leiko I.P., 1980a, *Opt. Spectrosc.*, **48**, 13
- Svyatkin I.A., Kuznetsova L.A., Kuzyakov Y.Y., 1980b, *J. Quant. Spectrosc. Radiat. Transfer*, **23**, 307
- Svyatkin I.A., Kuznetsova L.A., Kuzyakov Y.Y., 1980c, *J. Quant. Spectrosc. Radiat. Transfer*, **24**, 25
- Svyatkin I.A., Kuznetsova L.A., Kuzyakov Y.Y., 1982, *Opt. Spectrosc.*, **53**, 339
- Tam A.C., Happer W., 1976, *J. Chem. Phys.*, **64**, 2456

- Tatum J.B., 1967, *Astrophys. J. Suppl.*, **14**, 21
Telle H.H., 1984, *J. Chem. Phys.*, **81**, 195
Telle H.H., 1986, *J. Molec. Struct.*, **143**, 565
Tyte D.C., Hebert G.R., 1964, *Proc. Phys. Soc.*, **84**, 830
Vanpee M., Kineyko W.R., Caruso R., 1970, *Combustion and Flame*, **14**, 381
Vidal C.R., Stwalley W.C., 1982, *J. Chem. Phys.*, **77**, 883
Vidal C.R., Stwalley W.C., 1984, *J. Chem. Phys.*, **80**, 2697
Von Moers F., Heitz S., Busener H., Sagner H.J., Hese A., 1987, *Chem. Phys.*, **116**, 215
Way K.R., Stwalley W.C., 1973, *J. Chem. Phys.*, **59**, 5298
Wentink T., Pederson N., Diebold G., 1971, *Radiative Behaviour of Metal Oxides in Laser Blowoff*, DASA Report No 2704
West J.B., Broida H.P., 1975, *J. Chem. Phys.*, **62**, 2566
Whiting E.E., 1972, PhD thesis, York University, Toronto, Canada
Whiting E.E., Nicholls R.W., 1974, *Astrophys. J. Suppl.*, **27**, 1
Whiting E.E., Schadee A., Tatum J.B., Hougen J.T., Nicholls R.W., 1980, *J. Molec. Spectrosc.*, **80**, 249
Wine P.H., Melton L.A., 1976, *J. Chem. Phys.*, **64**, 2692
Wing R.F., Cohen J., Brault W., 1977, *Astrophys. J.*, **216**, 659
Woodward J.R., Hayden J.S., Gole J.L., 1989, *Chem. Phys.*, **134**, 395
Yarkony D.R., 1988, *J. Chem. Phys.*, **89**, 7324
Yerle R., 1979, *Astron. Astrophys.*, **73**, 346
Yoshimine M., McLean A.D., Liu B., 1973, *J. Chem. Phys.*, **58**, 4412
Zemke W.T., Stwalley W.C., 1978, *J. Chem. Phys.*, **68**, 4619
Zemke W.T., Crooks J.B., Stwalley W.C., 1978, *J. Chem. Phys.*, **68**, 4628
Zemke W.T., Way K.R., Stwalley W.C., 1978, *J. Chem. Phys.*, **69**, 402
Zemke W.T., Stwalley W.C., 1978, *J. Chem. Phys.*, **69**, 409
Zemke W.T., Stwalley W.C., 1980, *J. Chem. Phys.*, **73**, 5684
Zyrnicki W., 1975, *J. Quant. Spectrosc. Radiat. Transfer*, **15**, 575