

LABORATORY STUDIES OF POLYATOMIC COMETARY MOLECULES AND IONS

G. Herzberg

At present only four polyatomic molecules or ions have been identified in the spectra of comets and their tails. They are C_3 , CO_2^+ , NH_2 , and H_2O^+ . The first two are linear molecules. The C_3 radical gives rise to the well-known 4050 group. It was first obtained¹ in the laboratory in an interrupted discharge through CH_4 ; was definitely identified by Douglas² as being due to C_3 , and was later investigated in considerable detail in absorption³ in the flash photolysis of CH_2N_2 . The complicated vibrational structure of this spectrum was first understood when it was realized that the bending frequency in the ground state is very low (64 cm^{-1})^{3,4} and that in the excited state the interaction of the vibrational angular momentum with the electronic angular momentum leads to large splittings (Renner-Teller splittings)⁵.

The same kind of interaction of vibrational and electronic angular momentum occurs also in the ground state of CO_2^+ but up to now only a provisional analysis of this spectrum is available^{6,7}.

NH_2 and H_2O^+ are non-linear molecules. The spectrum of the first occurs in emission in oxyammonia flames and in absorption in the flash photolysis of ammonia^{8,9}, while the spectrum of the second was first obtained by Lew and Heiber¹⁰ in emission in a low pressure hot cathode discharge. The spectra of NH_2 and H_2O^+ are surprisingly similar to each other, consisting of progressions of bands in the red part of the spectrum which are alternately of the Σ and Π type. While in the lower state the molecule or ion is strongly bent with an angle of 103° and 110° respectively, in the excited state both are nearly linear. Some molecular data on H_2O^+ are given in the accompanying Table 1 supplied by Dr. Lew¹¹.

The first H_2O^+ lines identified in the spectrum of Comet Kohoutek were the lines at 6147.6, 6158.8 and 6200.1 Å observed by Herbig¹² and Benvenuti and Wurm¹³. They belong to the 8-0 Π band of H_2O^+ and represent the transitions with lowest K and N values¹⁴. Further spectra by Wehinger and Wyckoff and Herbig¹⁵ have shown some fifty further lines belonging to the 5-0, 6-0, ..., 10-0 bands. The alternation of band structure between even and odd vibrational quantum numbers of the upper state is clearly visible in these spectra. It is particularly the presence of the Δ bands near the Σ bands that makes the band structure for odd v_2 values so different. In Herbig's spectra the spin doubling in a number of "lines" is well resolved, leaving no doubt whatever in the identification of H_2O^+ in the tail of the comet.

Table 1

Rotational Constants of H_2O^+ (in cm^{-1})

$^2\text{B}_1$ Ground State (0,0,0)

$A = 29.040$	$D_K = 0.04338$
$B = 12.410$	$D_{JK} = -0.00392$
$C = 8.474$	$D_J = 0.00087$
	$D_2 = -0.000767$

$^2\text{A}_1$ Excited State

$5799.6\text{\AA} \quad \Sigma(0,9,0)$	$B = 8.77 \pm 0.01$
	$D = -0.0066$

$5494.7\text{\AA} \quad \left\{ \begin{array}{l} \Pi^+ \\ \Pi^- \end{array} \right\} (0,10,0)$	$\left\{ \begin{array}{l} B = 9.50 \\ B = 8.40 \end{array} \right.$
--	---

References

1. G. Herzberg, *Ap. J.* 96, 314 (1942).
2. A.E. Douglas, *Ap. J.* 114, 466 (1951); *Can. J. Phys.* 32, 319 (1954).
3. L. Gausset, G. Herzberg, A. Lagerqvist and B. Rosen, *Ap. J.* 142, 45 (1965).
4. A.J. Merer, *Can. J. Phys.* 45, 4103 (1967).
5. G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules", D. Van Nostrand Co. Inc., New York, 1966.
6. S. Mrozowski, *Phys. Rev.* 60, 730 (1941); 62, 270 (1942); 72, 682, 691 (1947).
7. J.W.C. Johns, *Can. J. Phys.* 42, 1004 (1964).
8. G. Herzberg and D.A. Ramsay, *J. Chem. Phys.* 20, 347 (1952).
9. K. Dressler and D.A. Ramsay, *Phil. Trans.* 251A, 553 (1959).
10. H. Lew and I. Heiber, *J. Chem. Phys.* 58, 1246 (1973).
11. H. Lew, to be published.
12. G.H. Herbig, *I.A.U. Circular* 2596 (1973).
13. P. Benvenuti and K. Wurm, *Astron. & Astrophys.* 31, 121 (1974).
14. G. Herzberg and H. Lew, *Astron. & Astrophys.* 31, 123 (1974).
15. P.A. Wehinger, S. Wyckoff, G.H. Herbig, G. Herzberg and H. Lew, *Ap. J.* 190, L43 (1974).

DISCUSSION

A. H. Delsemme: Well, I think that Dr. Herzberg has again demonstrated how fundamental his contribution has been to the understanding of the molecular spectra. We know it already.

Now, to be fair for the next talk, I think we can have a 3 to 5 minute discussion, no more. Yes?

M. Oppenheimer: First of all, are you in disagreement with what Wehinger has just said?

G. Herzberg: I am in disagreement with his point that the excitation is by photoionization. I believe that it is due to resonance fluorescence. I've had several discussions with Dr. Wehinger about this point, and I think we are perhaps converging.

I think one of the difficulties that perhaps he didn't quite appreciate, is that in the calculation of the intensities of these bands one has to use Franck-Condon factors that correspond to H₂O-plus only and not the Franck-Condon factors that are observed in the photoelectron spectrum of H₂O. When you start from the ground state say, H₂O, and go to the excited state of H₂O-plus, you get certain Franck-Condon factors. And they are definitely slightly different from those of H₂O-plus. The H₂O-plus ones are not so readily available, and this may be the reason for the discrepancy that Dr. Wehinger found between observed intensities and those calculated on the fluorescence mechanism.

M. Oppenheimer: Which is faster, the ionization of H₂O, or the excitation of H₂O-plus?

G. Herzberg: I would say that the excitation would be faster, but I'm only guessing. There are certainly people here in this group who would know that better than I do.

M. Oppenheimer: If the ionization is faster, and since H₂O was created by sublimation on the surface, then you should only see H₂O-plus created by direct ionization and never by resonance fluorescence.

G. Herzberg: Yes, but the trouble then is the H₂O⁺ in the tail, far in the tail, cannot come from H₂O in the tail. It's hard to assume that neutral H₂O is concentrated in the tail.

DISCUSSION (Continued)

Well, it could also be excited by photoionization the first time. What I'm saying is that in order even to account for the low temperature, it has to emit infrared radiation in order to keep the temperature down. And that requires that there is a transition to the ground state, then going up again, and so on.

Let me give another example. You know that N_2^+ is present in the comet tail, and I would predict that in N_2^+ you would find that the rotational temperature, is high, for the same reason that the apparent temperature in C_2 in the coma is hot, because it can't radiate infrared radiation.