FLUORESCENCE EXCITATION SPECTRA OF THE XeCl(B, C) STATES IN A SUPERSONIC JET

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An electric discharge in a mixture of He, Xe and Cl₂ (or CCl₄) followed by a supersonic expansion produces cold XeCl molecules and allows the fluorescence excitation spectra of the XeCl(B, C) states to be recorded. The vibrational spectroscopic constants ω_e and $\omega_e x_e$ as well as the 0° transition energy of the C state have been measured.

1. Introduction

The spectroscopy of the XeCl molecule has been studied extensively through emission spectra [1-9] or through excitation spectra of the collisional Xe-Cl pair [10]. These works have given much information on the X ground state, and on the B excited state responsible for the laser action. Moreover, the ground state has been studied by collisional experiments [11] and the spectroscopy of both the X and the B states are well known. For the C state, which is responsible for the emission around 345 nm and which is quasi-degenerate with the B state, the spectroscopy is doubtful. Indeed the absorption cross section from the X state to the C state is at least 10 times smaller than to the B state, and the fluorescence of the C state is predominantly to the A state, which is totally repulsive. Nevertheless, it is important to determine the position of this state in order to clearly understand the relaxation processes which occur in the collisional formation of the XeCl(B) state.

Up to now the XeCl(X-C) 0^{0} transition energy was uncertain, varying from -240 to 22 cm^{-1} as compared to the 0^{0} transition of XeCl(X-B) [1-10]. As in many cases (XeF [12], Hg₂ [13], ...), the spectroscopy of cold molecules obtained in a supersonic jet can give important information that cannot be obtained so clearly by other techniques.

2. Experimental

The difficulty of this experiment is due to the fact that the XeCl ground state is bound by only 300 cm⁻¹. The fairly unstable XeCl results from the reaction of excited Xe and chlorine-containing compounds. The usual technique for obtaining unstable species in a supersonic jet is the photodissociation of a parent molecule before the expansion; cold XeF [12] or OH [14] have been obtained this way. To avoid the use of an extra laser the reaction is initiated by dissociating the parent molecules with a highvoltage discharge prior to the expansion. The new molecules are subsequently formed by collisions of the fragments. This technique is certainly less clean than photodissociation, since it is not clear what kind of species are created by the discharge, but in the two systems we have looked at, we were able to observe the molecule of interest. Moreover, this method may be useful in creating more exotic species.

A schematic of the source is presented in fig. 1. The pulsed valve is a modified General Valve in which the stainless steel cap has been replaced by one of Vespel (Dupont) with an aperture of 1 mm. The O ring has been removed and gas tightness is simply provided by some teflon tape on the thread. After the aperture, the discharge chamber is made of teflon and is 4 mm long and 3 mm in diameter. The nozzle itself has a diameter of 0.5 mm. The discharge is obtained between two tungsten electrodes separated by 0.5 mm. One electrode is grounded and a

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Fig. 1. Schematic of the discharge and jet apparatus.

pulse of -6 kV for roughly 3 µs is sent to the other. The pulsed high-voltage power supply is home-made, and consists of a 2 μ F capacitor charged at 300 V, triggered by a triac which is discharged through a high-voltage transformer. In order to get a proper signal the right conditions have to be established. which depend on the nature of the gas mixture, on the distance between the electrodes, the backing pressure and the capacitance of the high-voltage circuit. Briefly, the discharge should not be too strong to avoid scattered light or vaporization of the electrodes. The timing between the discharge and the excitation laser is also very important: Under our experimental conditions a delay of 40 to 200 µs was necessary in order to observe the cold XeCl molecules. Some scattered light due to the discharge occurs during the first 20 µs, but no molecules have been observed at such a short time delay.

This system was first checked with OH, obtained by discharge through a $He-H_2O$ mixture (the water being held in a container at room temperature), and the cold OH (3 K) fragment was detected by laserinduced fluorescence with a signal-to-noise ratio greater than 100.

To obtain XeCl molecules a mixture of 0.5% Xe and Cl₂ in He was used. A mixture of 0.5% Xe in He and CCl₄ maintained at -30° C has also been used, the signal being two or three times smaller than with Cl₂.

The apparatus itself is composed of a vacuum chamber which is pumped by two root pumps (1000 m^3/h), which maintain the pressure at 0.1 Torr when a pressure of 5 atm is used before the expansion.

XeCl molecules are excited by a frequency-doubled dye laser (home-made) pumped by a YAG laser (BM Industrie) which crosses the supersonic jet 1 cm downstream. The fluorescence is filtered by a UG11 filter (Schott) and collected onto a C31000 RCA photomultiplier. The signal is averaged with a boxcar and digitized on a computer. Frequency calibration is carried out by comparison with Ne lines using a 0.75 m monochromator (Jobin-Yvon); the accuracy is 1 cm⁻¹.

3. Results

The excitation fluorescence spectrum of XeCl in the vicinity of the XeCl(B-X) 0^o transition is displayed in fig. 2. This spectrum has been recorded with an integrating temporal gate of +30, +130 ns in order to minimize the scattered light from the laser and to enhance the fluorescence of the C state (lifetime 131 ns [10]) as compared to the fluorescence of the B state (lifetime 11 ns [10]). The 0^o transition of X-B is clearly identified at 32495 ± 1 cm⁻¹ in good agreement with previous values [15]. On v' = 1 the isotopic splitting between Xe³⁵Cl and Xe³⁷Cl is



Fig. 2. Fluorescence excitation spectrum of cold XeCl. In order to enhance the fluorescence of the C state as compared to the B state a temporal gate of (30, 130 ns) is used. Backing pressure $p_0=4$ atm. Gas mixture: 0.5% Xe and Cl₂ in He.

clearly seen. 27 cm^{-1} to the red of the 0^o transition a small hot band is observed (fig. 2), which implies that the ground state vibrational frequency is 27 ± 1 cm^{-1} in good agreement with a previous value [15]. From the ratio of the hot band to the 0° transition we can conclude that the vibrational temperature in the ground state is about 16 K. The two weak peaks, -90 cm⁻¹ to the red and +114 cm⁻¹ to the blue of the X-B (0^{0}) , have been respectively assigned to the X-C (v''=0-v'=0 and v''=0-v'=1) transitions. This assignment is based on the previous studies which give the X-C (v'' = 0 - v' = 0) transition between -240 and +20 cm⁻¹ from the X-B (0⁰) transition. It is also confirmed by the isotopic splitting observed between Xe35Cl and Xe37Cl for higher vibrational levels as shown in fig. 3. Fig. 4 shows the isotopic splitting of the C state versus the quantum numbers: It clearly demonstrates that the assignment of the 0[°] transition is correct, since adding or removing one quantum of vibration would lead to a different isotopic splitting.

Fig. 3, recorded with the same gate on the boxcar integrator, also shows that the ratio of the intensity between C and B depends strongly on the excited vibrational level. Moreover, in fig. 2 it can be seen that the XeCl(X-C, v'=0-v'=1) transition is stronger than the 0°. This implies that the equilibrium distances of the B and C states are quite different, the C state equilibrium distance being shorter than that of the B state. Due to the weakness of the signal, a



Fig. 3. Fluorescence excitation spectrum of XeCl(X-B, C) v'' = 0 - v' = 5, 6, 7. Same experimental conditions as in fig. 2.



Fig. 4. Plot of the experimental isotopic shift of the XeCl(C) state. The dots represent the calculated values for different possible v' vibrational assignments.

Table 1 Vibrational spectroscopic constants (in cm⁻¹) of the B and C states of XeCl

	C state this work	B state	
		this work	ref. [15]
$\overline{\nu(0^0)}$	32405 ±1	32 495 ±1	32489
ω_{e}	204 ± 1	193 ±1	195.2
$\omega_e x_e$	0.75 ± 0.1	0.25 ± 0.07	0.54
T _e	32303 ±1	32398 ±1	32405

Franck-Condon simulation and a more quantitative measurement are meaningless.

The other difference between the B and the C states is the vibrational frequency: As can be seen on figs. 2 and 3 the vibrational frequency of the C state is larger than in the B state.

The spectroscopic constants ω_e and $\omega_e x_e$ for the B and C states, determined via a Birge-Sponer plot (up to v' = 7) derived from these spectra, are given in table 1.

4. Conclusion

This work shows that the supersonic jet technique in conjunction with a high-voltage electric discharge used to produce radicals is a useful method of studying the spectroscopy and reactivity of fairly unstable species.

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References

- J. Tellinghuisen, A.K. Hays, J.M. Hoffman and G.G. Tisone, J. Chem. Phys. 65 (1976) 4473.
- [2] J. Tellinghuisen and M. McKeever, Chem. Phys. Letters 72 (1980) 94.
- [3] P.S. Julienne and M. Kraus, Appl. Phys. Letters 35 (1979) 55.
- [4] K. Tamagake, D.W. Setser and J.H. Kolts, J. Chem. Phys. 74 (1976) 4286.
- [5] J.E. Velazco, J.H. Kolts and D.W. Setser, J. Chem. Phys. 65 (1976) 3468.

- [6] Y.C. Yu, D.W. Setser and H. Horiguchi, J. Chem. Phys. 87 (1983) 2199.
- [7] B.S. Ault and L. Andrew, J. Chem. Phys. 65 (1976) 4192.
- [8] J. Bokor and C.K. Rhodes, J. Chem. Phys. 73 (1980) 2626.
- [9] J. Le Calvé, M.C. Castex, B. Jordan, G. Zimmerer, T. Möller and D. Haaks, Photophysics and photochemistry above 6 eV, ed. F. Lahmani (Elsevier, Amsterdam, 1985) p. 639.
- [10] G. Inoue, J.K. Ku and D.W. Setser, J. Chem. Phys. 80 (1984) 6006.
- [11] C.H. Becker, J.J. Valentini, P. Casavecchia, S.J. Sibner and Y.T. Lee, Chem. Phys. Letters 61 (1979) 1.
- [12] D.L. Monts, L.M. Ziurys, S.M. Beck, M.G. Liverman and R.E. Smalley, J. Chem. Phys. 71 (1970) 4057.
- [13] A. Zehnacker, M.C. Duval, C. Jouvet, C. Lardeux-Dedonder, D. Solgadi, B. Soep and O. Benoist d'Azy, J. Chem. Phys. 86 (1987) 6565.
- [14] M.T. Berry, M.R. Brustein, J.R. Adamo and M.I. Lester, J. Phys. Chem. 92 (1988) 5551;
 M.T. Berry, M.R. Brustein and M.I. Lester, Chem. Phys. Letters 153 (1988) 17;
 W.M. Fawzy and M.C. Heaven, J. Chem. Phys. 89 (1988) 7030.
- [15] K.P. Huber and G. Herzberg, Molecular spectra and molecular structure, Vol. 4. Constants of diatomic molecules (Van Nostrand Reinhold, New York, 1979).