

MATRIX ISOLATION LASER RAMAN SPECTROSCOPY:
THE RAMAN SPECTRUM AND MOLECULAR STRUCTURE
OF XENON DICHLORIDE

D. Boal and G. A. Ozin*

The Lash Miller Chemical Laboratories
and Erindale College
University of Toronto
Toronto, Ontario

The technique of matrix isolation infrared spectroscopy has proven on numerous occasions to be an extremely powerful tool for determining vibrational frequencies and molecular structures of highly reactive species. The need for reliable Raman data on comparable systems is obvious.

We have now had sufficient success to be assured that the matrix isolation Raman technique is practicable and can yield important data provided the experiments are performed under closely controlled conditions.¹

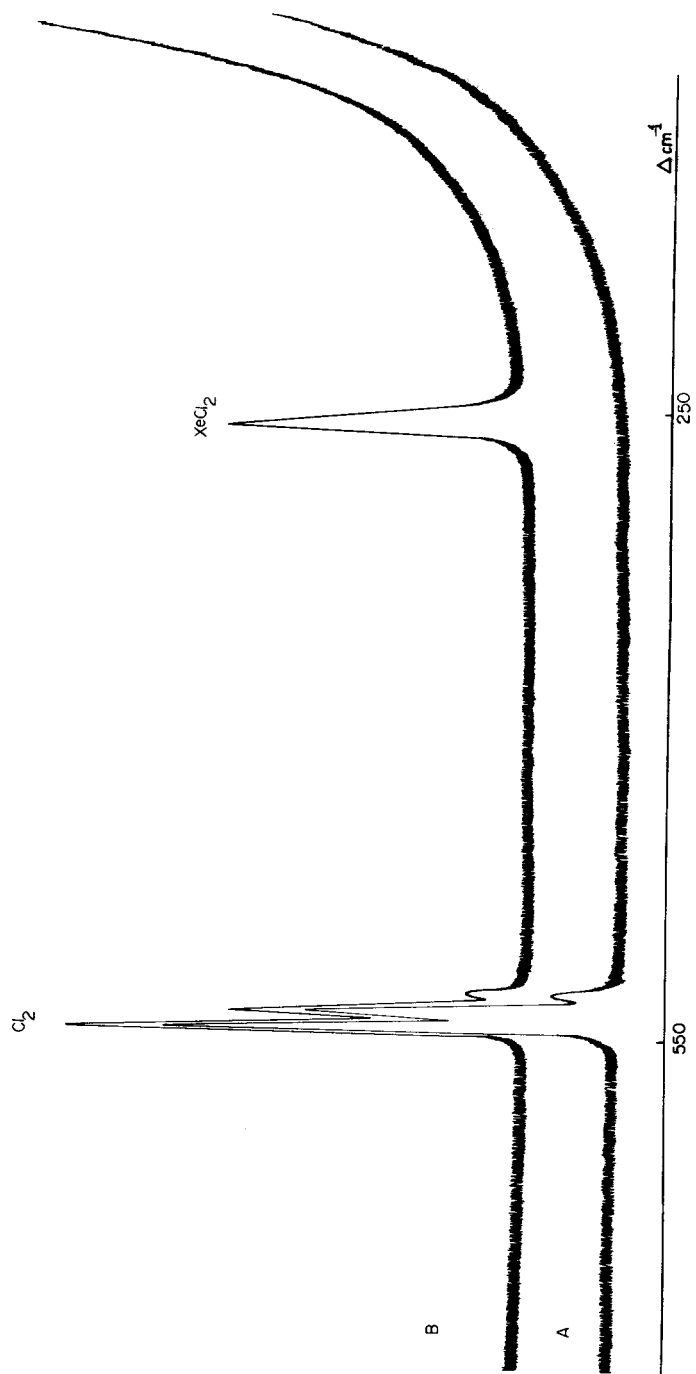
In this communication we report for the first time, matrix Raman data for xenon dichloride isolated in a xenon matrix. The investigation is part of a general study of the vibrational spectra and structures of highly reactive inorganic species that are formed in microwave discharges and then isolated at liquid helium temperatures.

Using methods similar to those employed by Meinert,² Nelson and Pimentel,³ a xenon-chlorine mixture (25:1) was passed through a microwave discharge (2450 mc, Microtron 200) and was condensed onto the cold tip (at 20°K) of a matrix Raman cell. The Raman spectrum of the matrix was recorded at 4.2°K on a Spex 1401 spectrophotometer.

A strong new band appeared at 253 cm^{-1} which was not present in the matrix isolated spectrum of chlorine done under identical conditions without the microwave discharge. Nelson and Pimentel⁴ have stated that they were unable to obtain trichlorine from discharging mixtures of chlorine and xenon, hence we assign the single strong band (apart from the stretching mode of diatomic chlorine) in the spectrum to xenon dichloride.[†]

The frequency of the band is characteristic of a totally symmetrical xenon-chlorine stretching mode. Further examination of the spectrum showed no other bands in the region $60\text{--}650\text{ cm}^{-1}$ proving that the species is linear and symmetrical ($D_{\infty h}$). The intensity of the new band relative to the chlorine band (see Figure 1) suggests that under the conditions of our matrix isolation Raman experiment, about half of the chlorine in the gas mixture is converted to xenon dichloride.

[†]In experiments with krypton and argon as matrix gases, the region around 250 cm^{-1} was perfectly clear.



The Raman spectra of a xenon-chlorine (25:1) matrix at 4.2°K

(A) without microwave discharge of the gaseous mixture, showing the presence of only Cl₂

(B) with microwave discharge of the gaseous mixture, showing the presence of both XeCl₂ and Cl₂.

D. BOAL AND G. A. OZIN

The asymmetric stretching frequency found in the matrix infrared spectrum³ for XeCl₂ (313 cm⁻¹) when taken in conjunction with the corresponding symmetrical stretching frequency from matrix Raman (253 cm⁻¹) yields xenon-chlorine bond stretching (f_r) and stretch-stretch interaction (f_{rr}) force constants of 1.34 and 0.01 md Å⁻¹ respectively. The relative magnitudes of the XeF and XeCl bond stretching force constants (2.85 and 1.34 md Å⁻¹ in XeF₂ and XeCl₂ respectively) reflects the anticipated weakness of the XeCl bond relative to the XeF bond.

We wish to emphasize in this preliminary report that we feel confident that matrix isolation Raman spectroscopy is a viable technique capable of yielding valuable information concerning many chemically important systems.

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References

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