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VIBRATIONAL PREDISSOCIATION SPECTRA AND DYNAMICS OF SMALL MOLECULAR CLUSTERS OF H_2O AND HF

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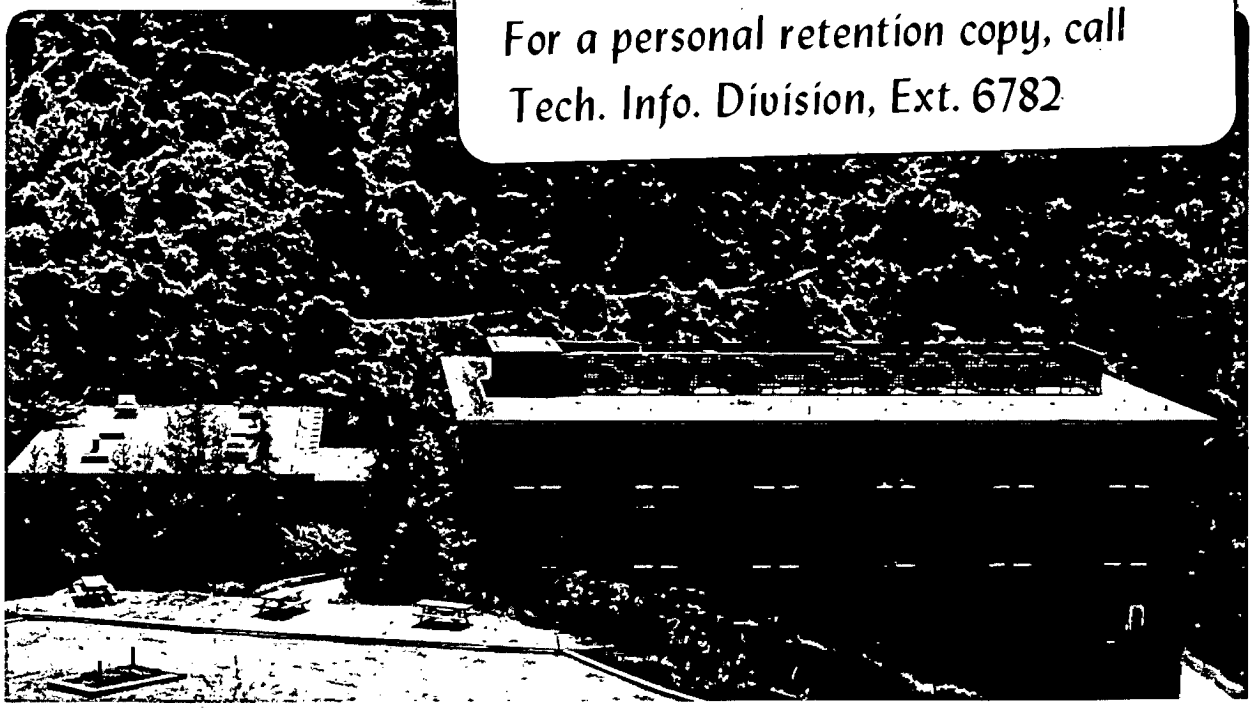

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ABSTRACT

Experimental results are presented on the vibrational predissociation spectra in the frequency range 3000-4000 cm^{-1} for the species $(HF)_n$ and $(H_2O)_n$, n = 2-6, using molecular beam techniques and a tunable infrared laser. The observed spectra show a dramatic change between the dimer and larger clusters which is thought to be a result of the cyclic structure of the trimer and larger clusters. The spectra are compared to calculated harmonic force constants of available intermolecular potentials to understand how these small, gas phase clusters relate to the liquid and solid phases of HF and H_2O. Additionally, the angular distributions of the predissociation products show that little energy appears as translational motion of the fragment molecules. This conclusion is consistent with recent theoretical models of the predissociation process. An upper limit of ~2 μsec is observed for the lifetime of the vibrationally excited clusters.

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INTRODUCTION

Van der Waals (VDW) molecules have long been suggested as a well defined, accessible model for studying the spectroscopic and dynamical properties of condensed phases. Hydrogen bonded liquids, in particular, have received much attention because of the noticeable spectroscopic changes which occur in the liquid and solid phases.[1] Despite the extensive study, little is known about the detailed electronic restructuring (potential energy surface) which is responsible for the large red shifts and intensity changes associated with hydrogen bonding.[1] Until the physical mechanisms for these changes are known, it will be difficult to parameterize analytical model potentials in an accurate and economical way. Indeed, most potential models proposed to date consist of simple atom-atom interactions which rarely predict more than one property correctly over a substantial range of conditions.[2] The experimental results presented below were measured in an attempt to understand the rate at which the bulk phase spectroscopic behavior is approached for these two molecules.

EXPERIMENTAL:

The $(H_2O)_n$ and $(HF)_n$ clusters are formed in an adiabatic expansion using neat or rare gas mixtures of HF and H_2O. The infrared radiation is obtained from a Nd:YAG pumped $LiNbO_3$ optical parametric oscillator (OPO) based on the L-shaped cavity design of Byer.[3] For the frequency range 3000-4000 cm^{-1}, the pulse energy is 1-4 mJ with a pump

energy fluence of 1 J/cm^2, and the linewidth (FWHM) varies from 3 to 4 cm^{-1}.

The predissociation of the clusters is detected in two different configurations using a mass spectrometer.

(A) Perpendicular Laser-Molecular Beam Arrangement

Figure 1 shows an in-plane view of this experimental configuration. The vibrational predissociation is observed by monitoring the appearance of the predissociation fragments. The electron bombardment ionizer-mass spectrometer assembly rotates on a 20 cm radius circle about the intersection point of the laser and molecular beams. The defining apertures in the mass spectrometer limit the detector's line of sight to a 3 mm x 3 mm region at the intersection point. Clusters that predissociate before travelling beyond this viewing region (nominal residence time is 2 μsecs) and whose fragments recoil into the detector, are detected as an increase in the ion signal at the masses characteristic of the cluster predissociation fragments. The predissociation signals are collected by a multi channel scaler triggered by the laser pulse and accumulated for 2,000-10,000 laser pulses. The laser power is monitored by a power meter placed after the intersection region. The power dependence of the signal is measured to insure that the predissociation yield is linear with photon number. The angular distribution of the predissociation fragments is used to determine the translational energy distribution of the product molecules.[4]

(B) Coaxial Laser-Molecular Beam Arrangement

A cross sectional view of this apparatus is shown in Fig. 2. Here, the laser and molecular beams are superimposed while the mass spectrometer monitors the molecular beam. Vibrational predissociation is observed as depletion in the signal of the parent cluster mass. Compared to the perpendicular arrangement, this method has thirty times the interaction volume between the laser and molecular beams, and detects all predissociation events in contrast to the small fraction sampled by the perpendicular arrangement. The increase in the detectable signal ($\sim 10^6$) permits the use of 1.0 to 0.1% seeded beam ratios (HF or H_2O in a He or Ar carrier) and faster data acquisition. However, it cannot supply angular distribution information.

RESULTS

Vibrational predissociation spectra of $(H_2O)_n$ and $(HF)_n$ are displayed in Figs. 3-6. The angular dependence of the $(H_2O)_n$ predissociation fragments is shown in Fig. 7. Similar results were obtained for $(HF)_n$. The narrow angular range of the products ($\theta \leq 10°$) indicates that little of the excess energy appears as product translation. The steep monotonic decrease in the angular data with increasing laboratory angle can only be fit by a product translational energy distributon which peaks at or near zero degrees. The excess energy thus remaining after the cluster dissociates must be in the internal degrees of freedom of the fragments.

For energetic reasons[5] the dominate predissociation channel for both $(HF)_n$ and $(H_2O)_n$ is thought to be

$$(H_2O)_n + h\nu \rightarrow (H_2O)_{n-1} + H_2O \quad (1)$$

$$(HF)_n + h\nu \rightarrow (HF)_{n-1} + HF \quad (2)$$

since this is consistent with the observed independence of the shape of the angular distribution with OPO frequency. The electron bombardment ionization complicates assigning the signal observed at a particular mass peak to a specific cluster. The dominate ionization channel is most probably

$$(H_2O)_n + e^- \rightarrow (H_2O)_{n-1}H^+ + OH + 2e^- \quad (3)$$

$$(HF)_n + e^- \rightarrow (HF)_{n-1}H^+ + F + 2e^- \quad (4)$$

However, the channels

$$(H_2O)_n + e^- \rightarrow (H_2O)_{n-m}H^+ + \ldots \quad (5)$$

$$(HF)_n + e^- \rightarrow (HF)_{n-m}H^+ + \ldots \quad (6)$$

with $m > 1$ are also observed to occur. Figure 3 (a), (e) shows two frequency scans at the H_3O^+ mass under two different source conditions. The changes observed for the two different cluster distributions are a result of the larger cluster predissociation fragments from process (1) ionizing by the channel (5) with $m > 1$. In cases where

several clusters absorb at the same frequency, varying the source pressure, seeding ratios, and recording the spectra at many masses can distinguish which bands belong to different polymers.

DISCUSSION

From the data displayed in Figs. 3-6, it is obvious that the dimer species $(H_2O)_2$ and $(HF)_2$ are substantially different compared to the larger clusters. Molecular beam electric resonance spectroscopy has established the ground vibrational state structures of $(H_2O)_2$,[6] and $(HF)_2$.[7] The three $(HF)_2$ bands are assigned to the HF stretch of the hydrogen bonded proton (3720 cm^{-1}), the HF stretch of the "free" proton (3878 cm^{-1}), and a combination band involving an intra- and inter-molecular vibration (3970 cm^{-1}). The $(H_2O)_2$ bands are similarly assigned to free (3715, 3625 cm^{-1}) and hydrogen bonded (3596, 3524 cm^{-1}) protons. The bands at 3715 cm^{-1} and 3500 cm^{-1} are also seen in the spectra of larger water clusters. Their presence at the dimer parent mass could be from the larger neutral cluster ionizing via eqn. 5. More detailed studies will be necessary to measure unambiguously the complete $(H_2O)_2$ spectra in this region.

The $(HF)_n$ and $(H_2O)_n$, n = 3-6 clusters exhibit a strong, broad, red shifted band structure which is assigned to the hydrogen bonded protons. The lack of any absorption peaks above 3500 cm^{-1} for the $(HF)_n$, n = 3-6, clusters indicates the absence of a terminal ...H-F or ...F-H molecule. Consequently, these larger clusters must be cyclic.

Similarly, the absence of a band at 3596 cm^{-1} for the larger water clusters is consistent with a cyclic geometry for these clusters. The sharp, narrow peak at 3715 cm^{-1} is assigned to the "free" hydrogens which point away from the ring. Typical minimum energy water polymer structures predicted by available intermolecular potentials are shown in Fig. 8 and agree with this assignemnt of the observed spectra. Molecular beam deflection experiments for the larger $(HF)_n$,[7] and $(H_2O)_n$,[6] clusters indicate small to undetectable dipole moments for these species, as would be expected for cyclic structures.

The band structure of the hydrogen bonded absorption seems to be best described as a progression of combination bands. The equation

$$\nu^{obs} = \nu^{intra} + m\nu^{inter}, \quad m = 0,1,2 \tag{7}$$

where ν^{intra} is the fundamental frequency of the hydrogen bonded intra molecular H-F(HO) stretching motion, ν^{inter} a frequency of the intermolecular F--HF (O---HO) hydrogen bond, and ν^{obs} the observed bands are consistent with the more advanced treatments of hydrogen bonding. For the $(HF)_n$ series, the decrese of ν^{intra} and increase of ν^{inter} with increasing cluster size is in accordance with progressively weaker intramolecular bonds and stronger intermolecular bonds in the larger clusters.

The question arises, why are the hydrogen bonded protons of the cyclic structure so red shifted as compared to the dimer species? Since the dimer absorptions are characteristic of the pair interaction

potential, it might be a consequence of the change in the reduced mass of the proton motions in the cyclic as opposed to the open dimer configuration.

To investigate this possibility, the harmonic vibrational frequencies at the minimum energy configurations of the $(H_2O)_n$ polymers were calculated using 3 widely used potentials.[8,9,10] The harmonic frequencies of the polymer vibrations were multiplied by a constant choosen to bring the calculated monomer vibrational frequencies into close agreement with the known vibrational frequenices of H_2O. This was meant to serve as a crude correction factor for anharmonicity. The best agreement in all cases was from the Watt's potential[8] which uses the known gas phase H_2O anharmonic vibrational potential to describe the intramolecular forces. The polarization[9] and central force[10] models of Stillinger do not predict the appropriate tight grouping of the free OH peaks, and also indicate blue shifts relative to the monomer. These discrepancies are expected since no particular attention was paid to predicting the high frequency proton vibrations. The Watt's potential predicts the observed dimer spectra quite accurately given the approximations of the normal mode treatment and the type of data used to derive the intramolecular potential, namely 2nd virial coefficients and solid state nearest neighbor distances. When this pair potential is applied to larger clusters, the calculated spectra show two band groups - the free and hydrogen bonded protons. The calculated frequenices of the larger clusters are more commensurate with the observed and calculated dimer bands than the red shifts observed in the larger clusters. We

conclude that the pair potential cannot account for the red shifts, which must then be a result of non additive interactions. When an OH group is involved both in donating and accepting a hydrogen atom for hydrogen bonding, the electronic structure of that OH bond is significantly perturbed beyond that accountable by pair interactions.

An interesting implication of our assignments is how they suggest that past explanations for the infrared structure of liquid water are in error.[11] The basic conclusion of these previous studies was to assign each observed (or deduced) band to a different local environment. The present work, along with theoretical treatments by Rice and Sceats,[12] Marechal[13] and others,[14] suggests that the broad band structure is intrinsic to the hydrogen bond. Recent studies by Byer et al.[15] on the depolarization CARS spectra of liquid water have shown similar structure in the wavelength region of this study.

Two aspects of the predissociation dynamics were also observed in our experiments, an upper limit to the vibrational predissociation lifetime of the cluster, and the partioning of energy between translational and internal degrees of freedom of the predissociation products. The lifetime was determined by our observations of predissociation (in collision free conditions) in the perpendicular beam arrangement, and the agreement obtained between spectra measured by the two experimental configurations. Although the information from the product angular distribution is limited, it is possible to understand why little energy appears as translation and why the shape of the angular distributions are independent of the photon energy for the range probed (9-10.5 kcal).

Calculations were performed of the locally adiabatic predissociation (LDP) paths using the Watts potential for the dimer, trimer, and tetramer as shown in Fig. 9. The dimer path is straightforward, and similar to a diatomic molecule dissociation. The trimer path indicates a two step process. First, the separation of two oxygen atoms from ~2.75 Å - 5.50 Å breaks the cyclic structure to form an open chain, then a terminal monomer molecule dissociates with a curve similar to the dimer. The tetramer indicates more exotic behavior depending on the order with which the water molecules are separated. This is a result of numerous local minima on the potential surface. (The LDP's were generated by small sequential displacements of ~0.2 Å of the oxygen-oxygen distance, so the curves do not represent global minima).

These paths indicate that the geometry of the cluster when it dissociates is far removed from the equilibrium configuration of the separated products. Many low frequency vibrational motions will be excited in the cluster frgments left in these extended orientations. This would explain why little energy appears in translation, and why the product energy distribution should not depend dramatically on which motions are excited by the photon.

CONCLUSIONS

A preliminary study of the fundamental hydrogen atom vibrations in small clusters of HF and H_2O have indicated that the key to understanding the origins of the dramatic spectral changes induced by hydrogen bonding is in the differences between the dimer and larger clusters. Accurate quantum mechanical calculations of the electronic structure should be possible for these systems. These new results will then enable more accurate analytical potential functions suitable for modeling solution behavior.

The predissociation lifetime (<2 μsecs) and energy partioning among the product degrees of freedom were also obtained. The large geometry changes the trimer and larger clusters must undergo during dissociation appears to explain the small amount of energy released in translation and the insensitivity of this product energy to the range of photon energy these experiments.

Future experiments on isotopically substituted clusters should further the understanding of the dynamic coupling present in these clusters. A study of the behavior of larger clusters should also indicate whether it is possible to increase the cluster's heat capacity to the range where the predissociation can be measured in real time, if indeed the energy is substantially redistributed within the cluster before dissociation.

ACKNOWLEDGMENT

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5. Calculations of the dissociation energy, D_e, of water clusters using a variety of intermolecular potentials indicates this process (Eqn. 1) is always allowed. Dissociation into non monomeric products is not allowed over the complete frequency range probed for these same potentials.

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FIGURE CAPTIONS

Fig. 1. In plane view of perpendicular laser molecular beam apparatus. Labeled components are: 1) 0.007 in. diameter quartz nozzle heated to 125°C, 2) first skimmer, 3) second skimmer, 4) third skimmer, 5) power meter, 6) Germanium filter, 7) ionizer assembly, 8) quadrupole mass spectrometer. θ measures the angle of rotation of the detector from the molecular beam.

Fig. 2. Side view of the coaxial laser-molecular beam apparatus. Labeled components are: 1) BaF_2 entrance window for the OPO beam, 2) quadrupole mass spectrometer, 3) ionizer assembly, 4) final molecular beam defining aperture, 5) second skimmer, 6) first skimmer, 7) nozzle.

Fig. 3. Water cluster and condensed phase spectra. Panels (a)-(e) are spectra observed in the present work.

Fig. 4. Vibrational predissociation spectra of $(H_2O)_2$ and $(H_2O)_3$ obtained by the coaxial method.

Fig. 5. Vibrational predissociation spectra of $(HF)_n$, n = 3-6, corrected and normalized for photon number. The peaks marked with asterisks in the m/e = 41 spectrum are from $(HF)_3$, the other peaks are due to larger clusters.

Fig. 6. Vibrational predissociation spectrum of $(HF)_2$ corrected and normalized for the photon number, with the structure of $(HF)_2$ as determined by molecular beam electric resonance spectroscopy.

Fig. 7. Laboratory angular distributions for the detected mass ○ - H_3O^+; + - $(H_2O)_2\ H^+$; □- $(H_2O)_3\ H^+$; ●- $(H_2O)_4\ H^+$.

Fig. 8. Minimum energy cluster geometries for the Watts potential energy function (a,b,d,e,f), for the polarization model trimer (c), and for the configuration characterizing a transition state for the tetramer dissociating into a trimer and a monomer (g).

Fig. 9. Locally adiabatic dissociation energy curves for A. $(H_2O)_2 \rightarrow 2H_2O$, B. $(H_2O)_3 \rightarrow (H_2O)_2 + H_2O$, C. $(H_2O)_4 \rightarrow (H_2O)_3 + H_2O$ when adjacent hydrogen bonded waters are separated, D. $(H_2O)_4 \leftarrow (H_2O)_3 + H_2O$ when it is formed from a monomer adding to a cyclic trimer, E. $(H_2O)_4 \rightarrow (H_2O)_3 + H_2O$ when opposing non-hydrogen bonded water molecules of the cyclic tetramer are separated.

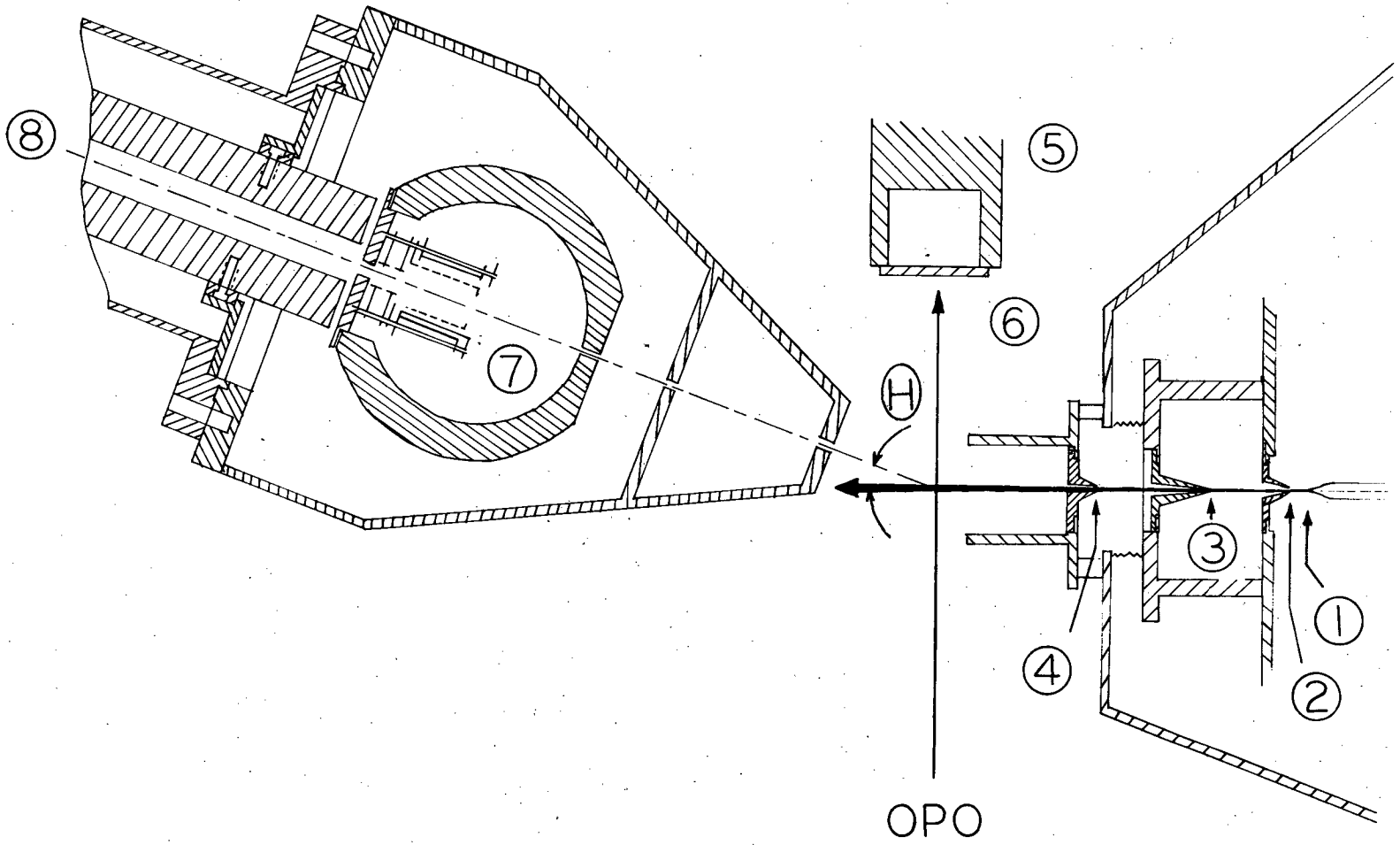

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Fig. 1

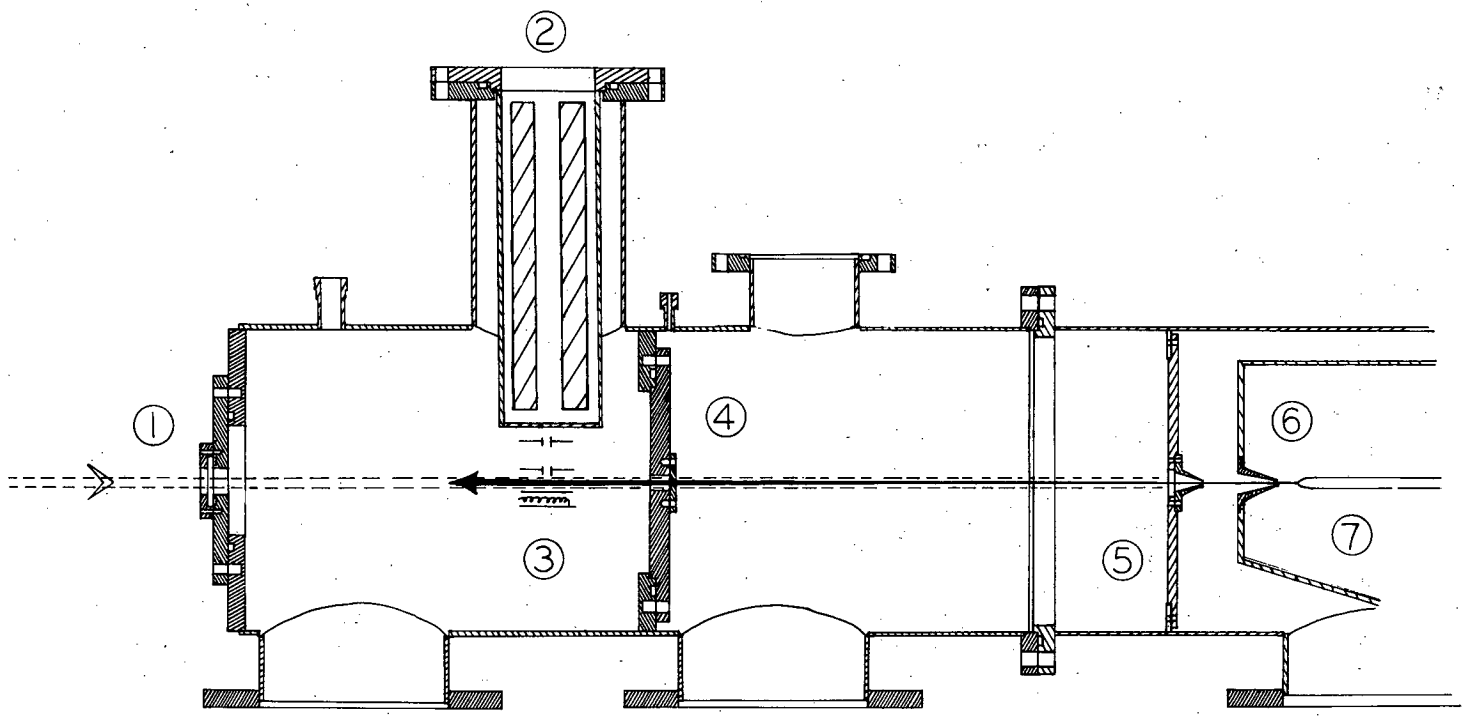

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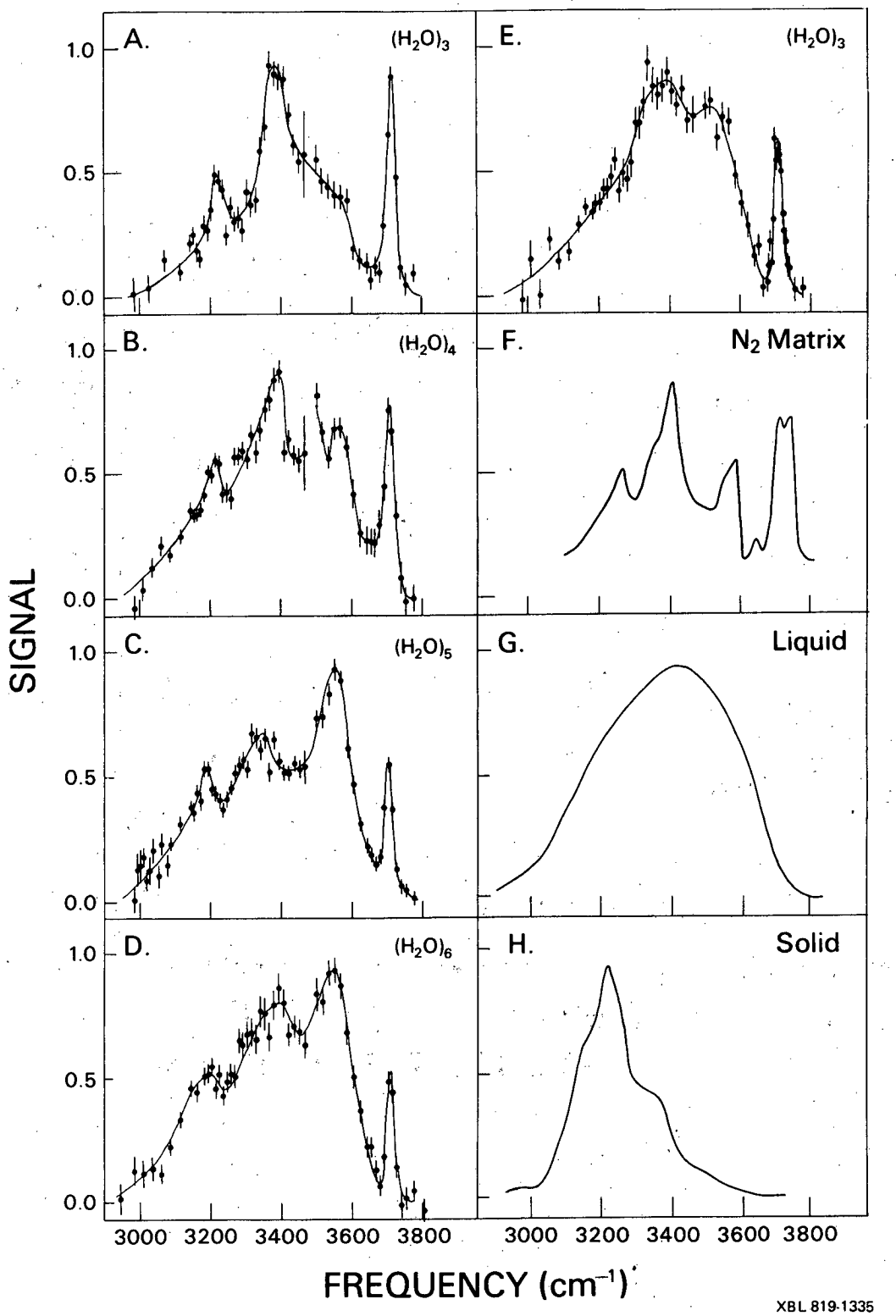
Fig. 2


A.
$(H_2O)_3$
B.
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C.
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F.
N_2 Matrix
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Fig. 3

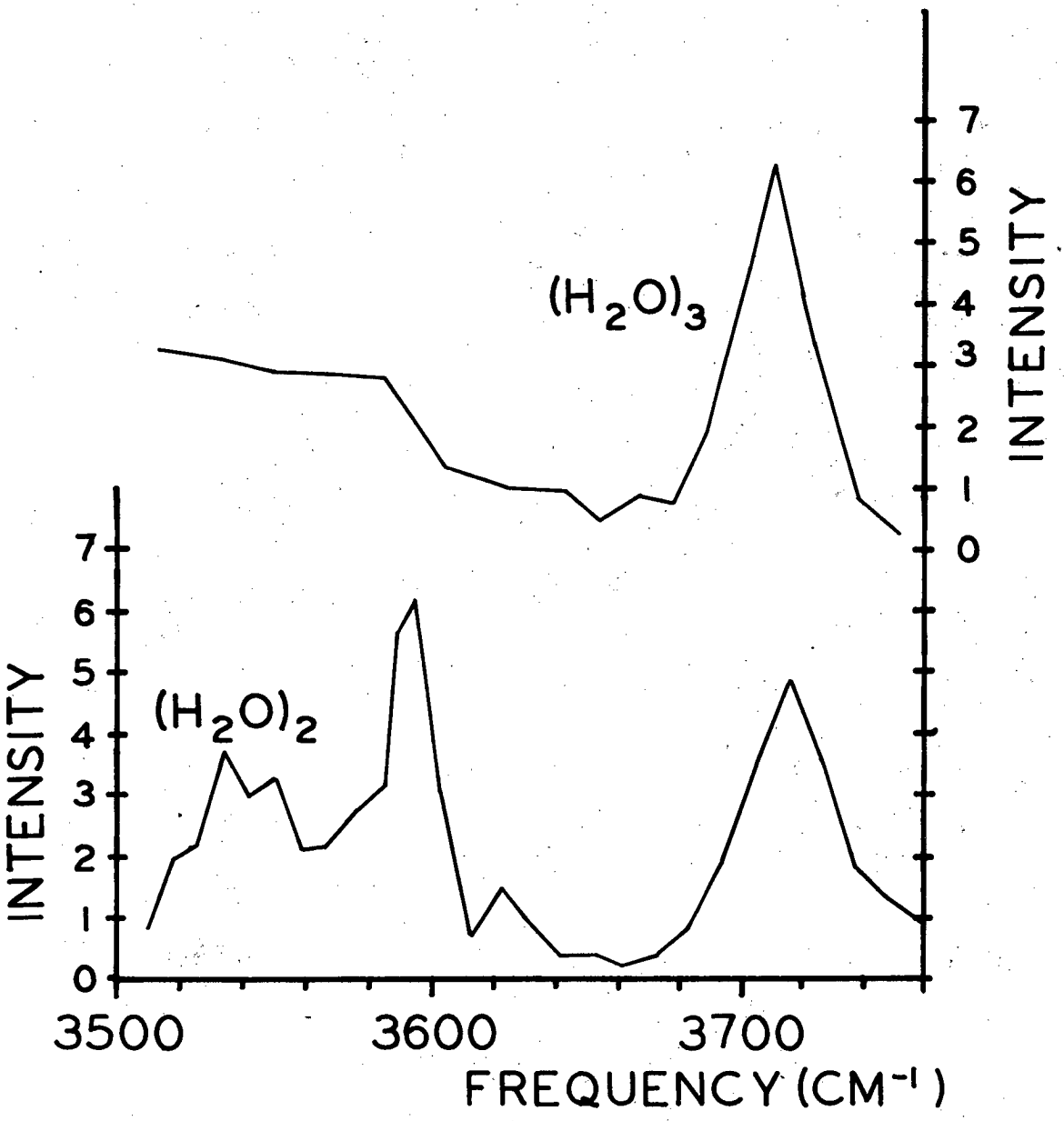

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Fig. 4

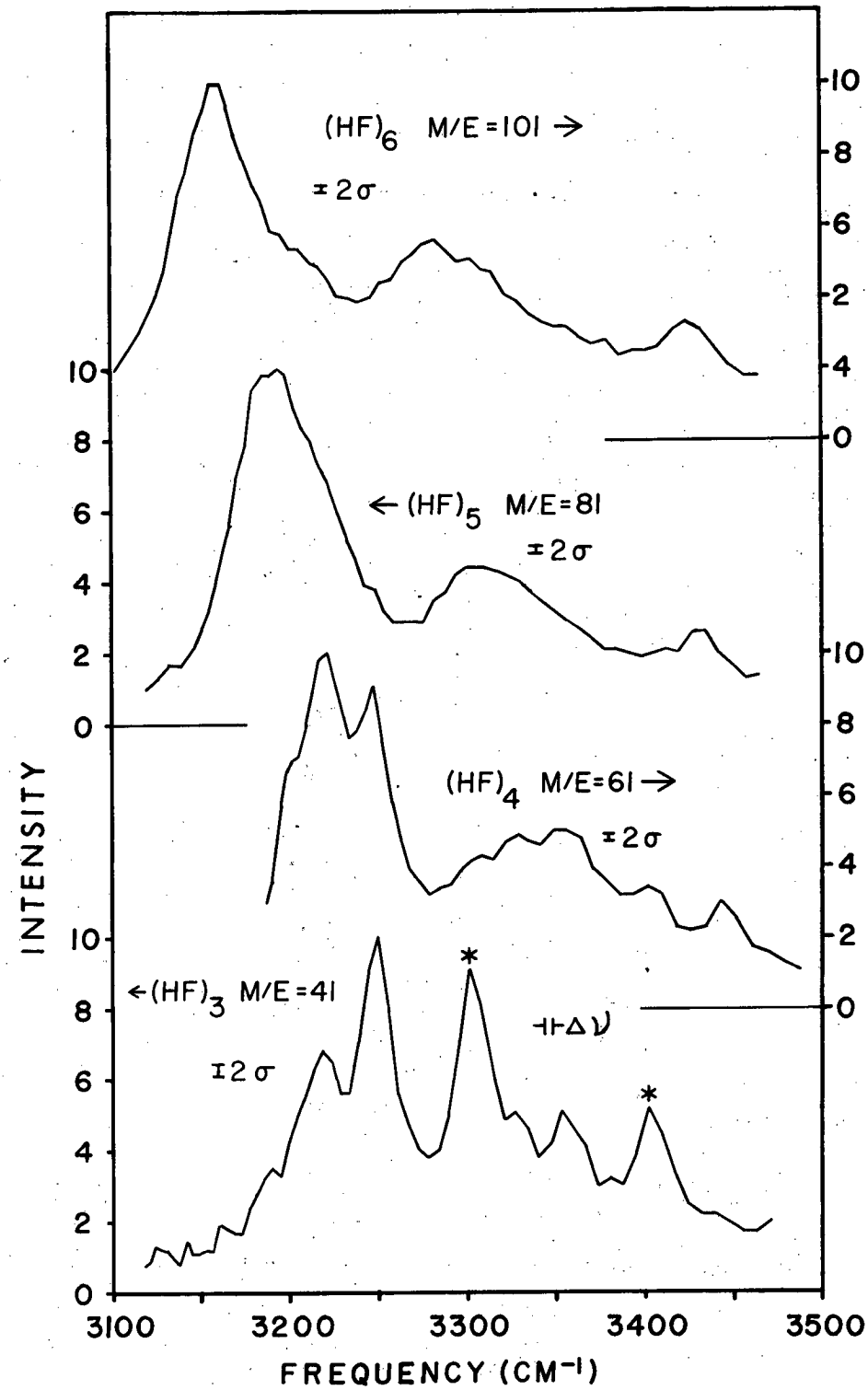

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Fig. 5

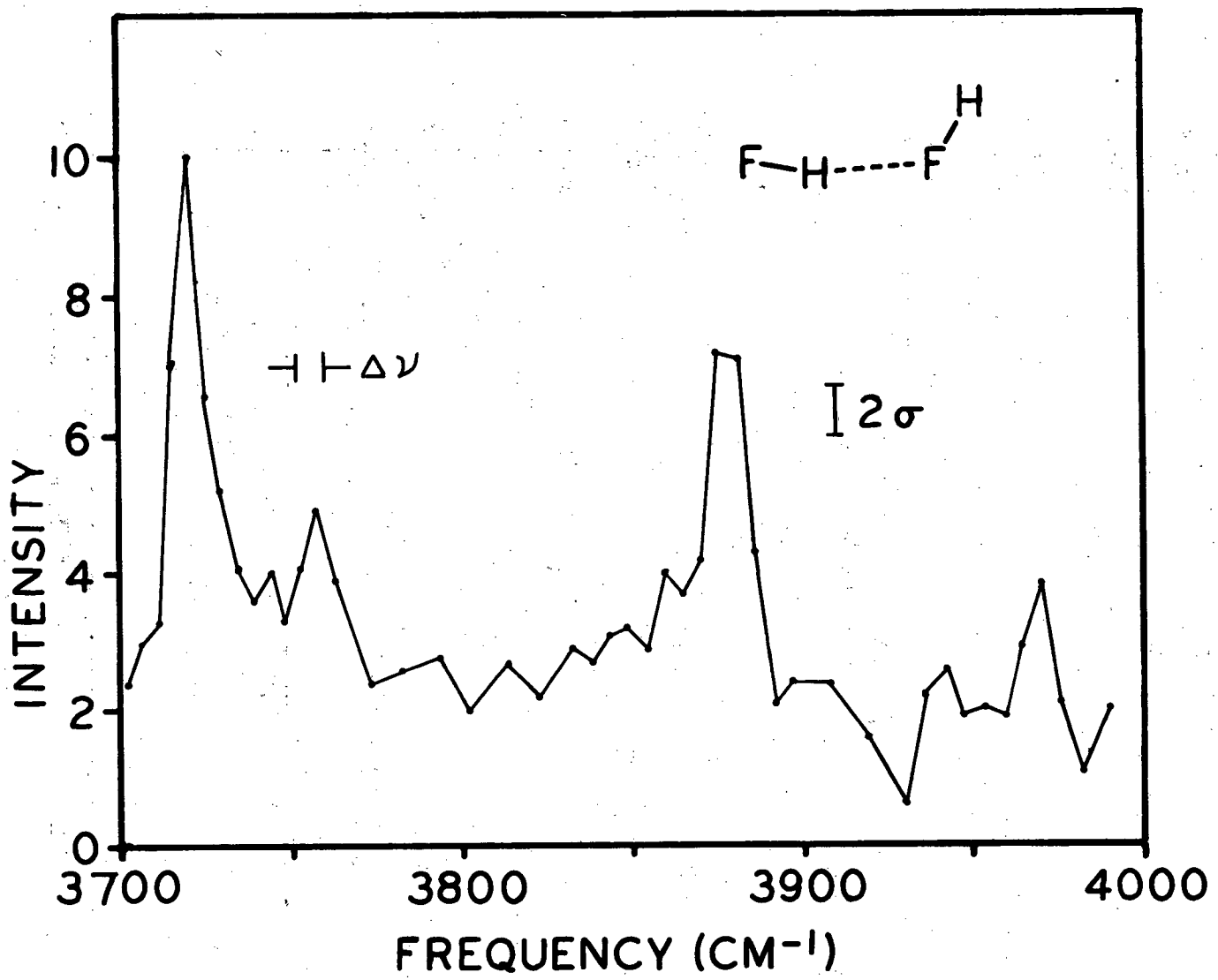

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Fig. 6

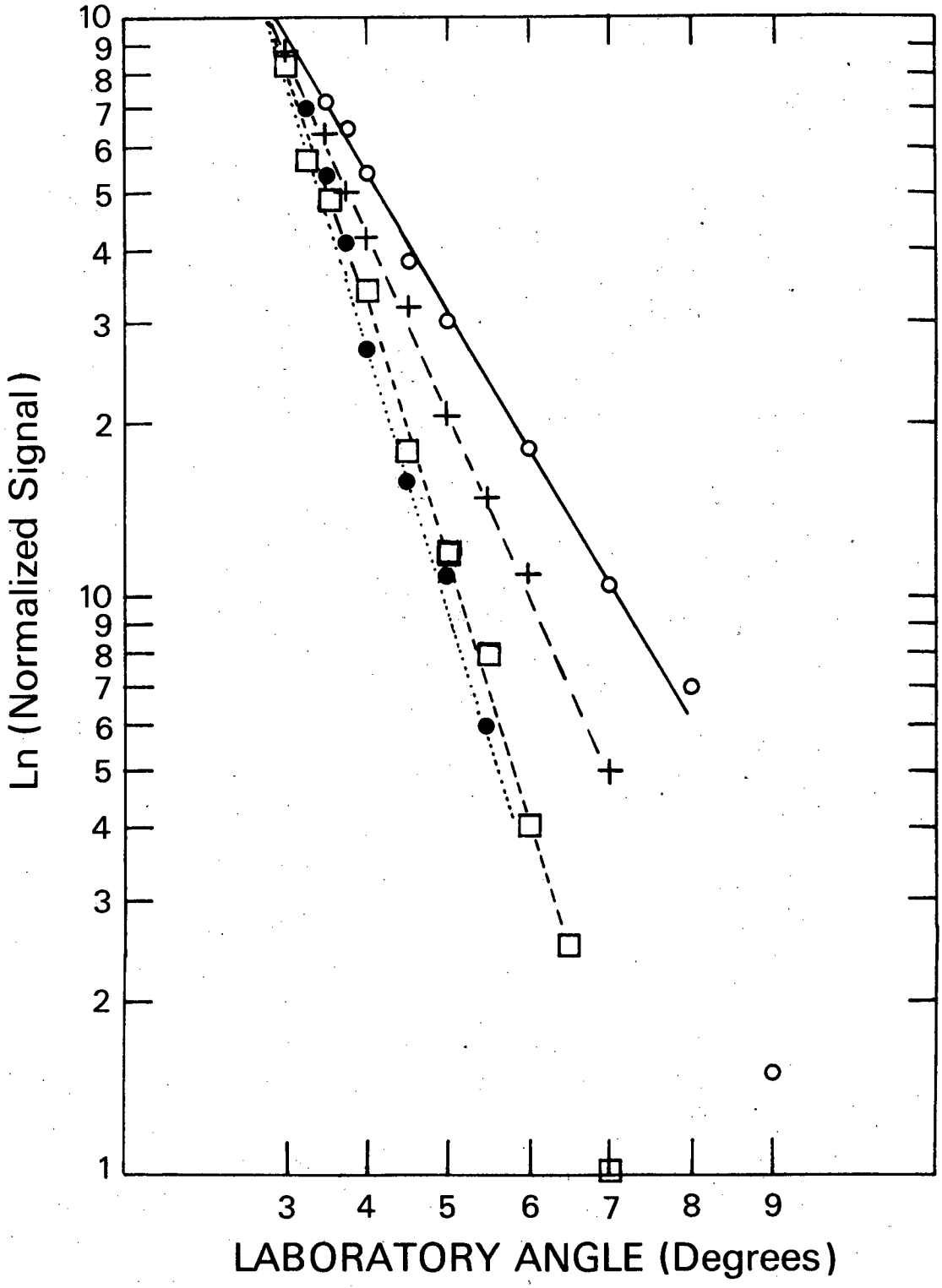

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Fig. 7

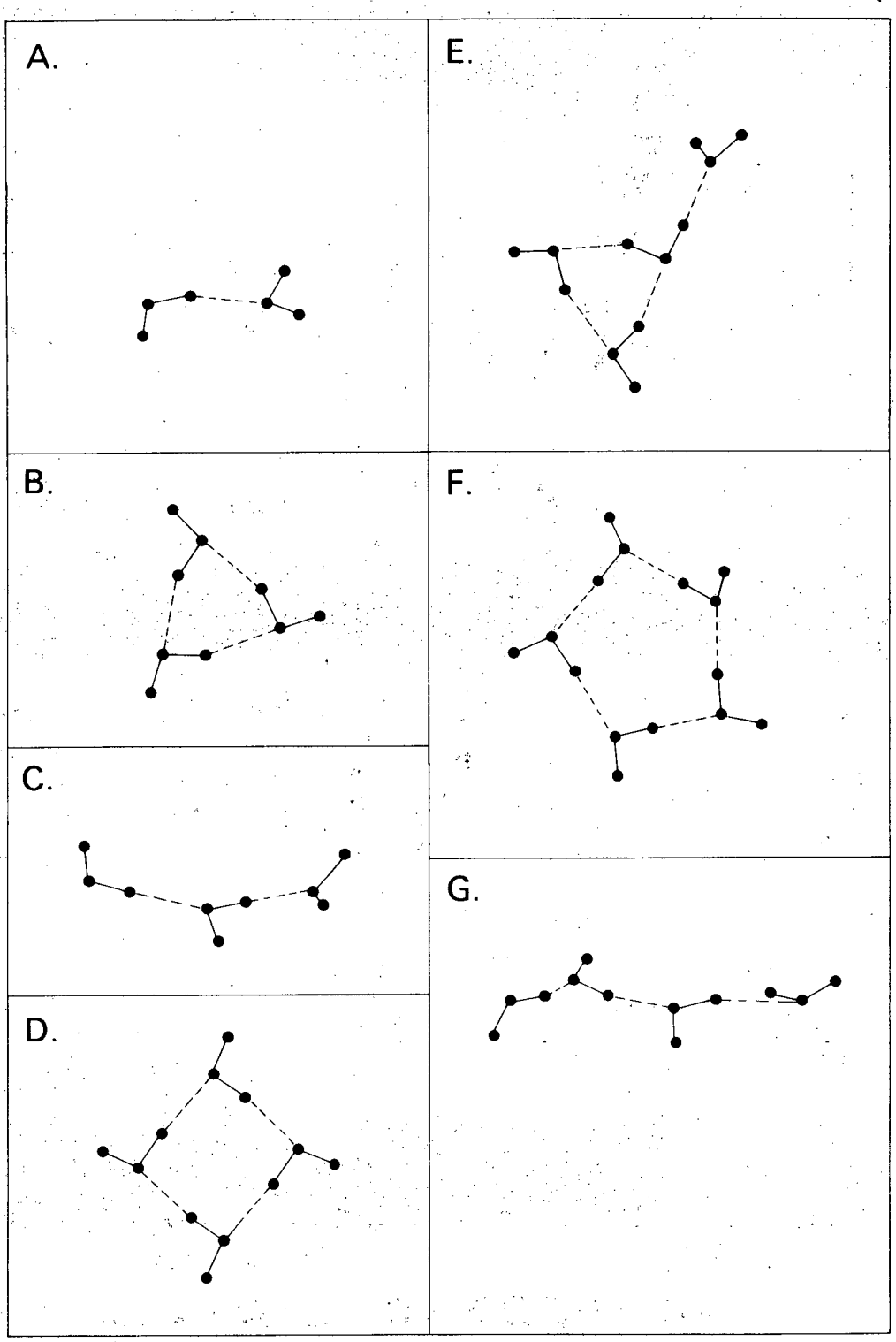

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Fig. 8

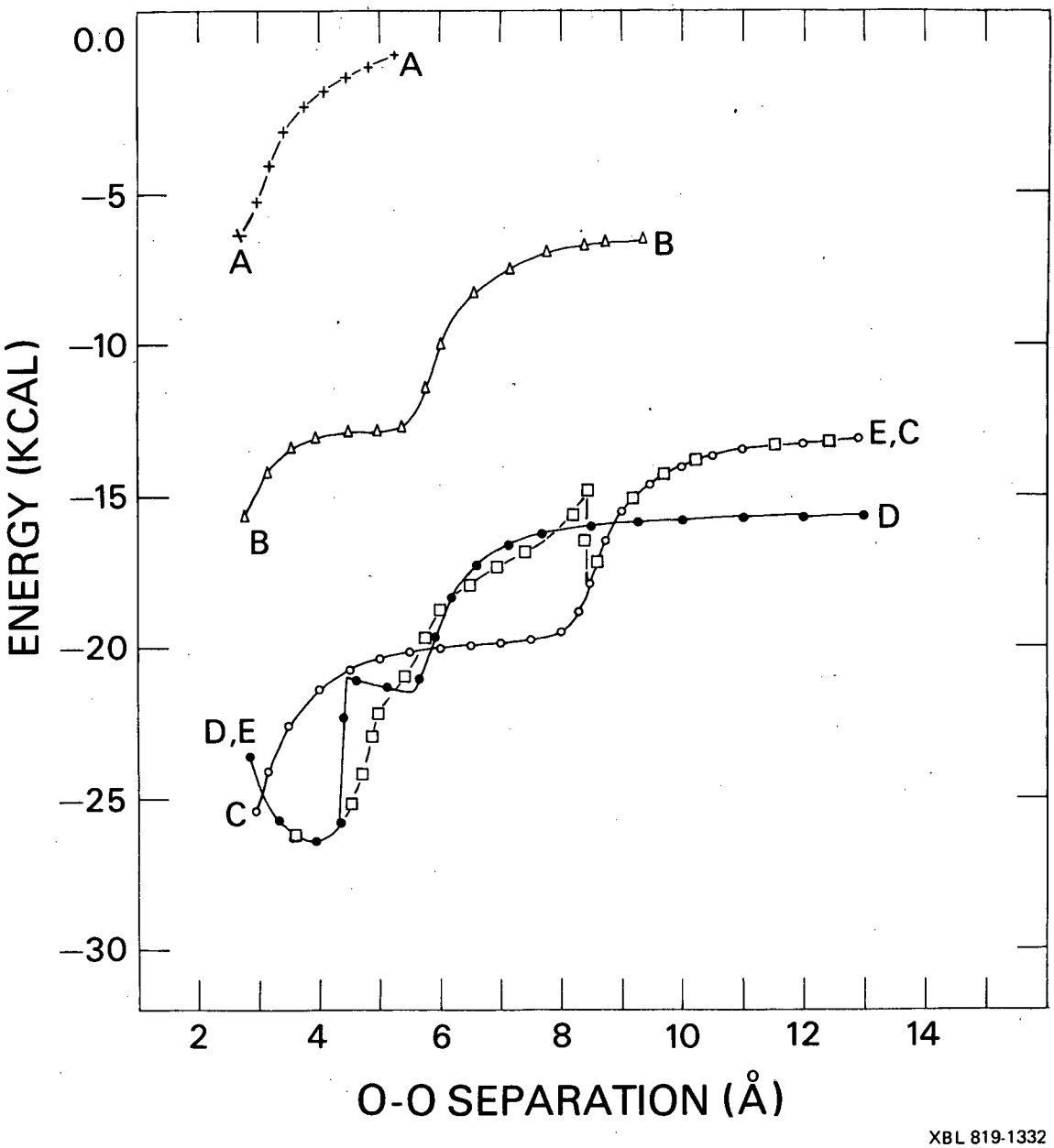
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Fig. 9

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