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Resonance Ionization Spectroscopy of Molecules, Clusters, and Ions

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Abstract

High resolution photoionization and fluorescence excitation spectra of dimers of the aromatic molecule fluorene $(C_{13}H_{12})_2$ reveal complex excitonic interactions. Comparison of results for isotopically pure and isotopically mixed dimers provide the information necessary to analyze the spectra in terms of intermolecular motion on two perturbed adiabatic potential surfaces. The intermolecular force field on the lower surface is characterized by a perturbed quartic potential, whereas the upper surface is characterized by a displaced quadratic potential. The results provide the first detailed experimental description of strong coupling between an intermolecular coordinate and the excitonic state of a molecular dimer.

INTRODUCTION

The understanding of electronic states of molecular dimers has been an elusive, but highly important goal, dating back to the origin of molecular spectroscopy and quantum chemistry. The idea is appealing and important because the electronic structure of the monomer components provide an ideal basis for interpretation of the more complex dimer. Therefore, when the intermolecular interactions are relatively weak, it should be possible to treat the dimer states in terms of products of monomer quantum states. The problem is complicated by the fact that the electronic product states for the dimer are degenerate, and therefore, they can be strongly coupled by intermolecular motion. This causes a breakdown in the Born-Oppenheimer approximation, which is normally used to separate nuclear and electronic motions. Thus, a study of the dimer problem can reveal aspects of Born-Oppenheimer coupling that are critical to spectroscopic and chemical problems.

Up until now, observed dimer spectra have not exhibited the features that are critical to the dimer problem. The systems studied to date were recently reviewed by Bernstein.[1] None of the molecular systems, including benzene, naphthalene, and pyrazine dimers, show significant evidence for coupling between electron motion and the intermolecular coordinates.

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[1] E. R. Bernstein, *Atomic and Molecular Clusters,* Elsevier, Amsterdam (1990).

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Limiting cases were theoretically outlined many years ago. In the case of weak excitonic interaction, vibrational levels of the monomer should be split into two components, with energy splittings roughly proportional to the intensity of the transitions. The existing examples conform to this case, however, due to molecular orientations or weakness of interactions, only one component has been resolved, corresponding to each monomer transitions. Intermolecular vibrational sidebands were either weak or missing. In the case of strong excitonic interaction, two separate potential surfaces are expected, corresponding to the two separate excitonic electronic states. These will have separate intermolecular vibrational manifolds.

The situation is expected to be more complicated when intermolecular vibrational coordinates participate in the interactions. They contribute additional degeneracies. So far, there are a number of systems that are presumed to have strong interactions involving intramolecular vibrations, however their spectra are unresolved, thereby hiding the underlying complexity. As described below, the fluorene dimer represents an ideal case to elucidate excitonic interactions in a dimer. The electronic coupling is moderately strong in the origin system, resulting in separated potential surfaces, and the intermolecular vibrational structure is highly resolved, permitting analysis of the spectra.

The electronically excited fluorene dimer is also representative of the general tendency of aromatics to form excimer state. Following excitation to the excitonic states, which are closely related to the states of the isolated monomer, the dimer undergoes transformation to much more tightly bound excimer states. Excimer states are thought to be repulsive in the ground electronic state, thus their fluorescence emission is spectrally broadened and greatly shifted to the red, relative to the excitonic absorption spectrum. Excimer states of large aromatic molecules were discovered more than two decades ago. They have been studied extensively in solution media. Over the years, attempts have been made to identify the electronic states responsible for excimer formation. Initially, it was suggested that excitonic type interaction between the monomers leads to the excimer stabilization. Charge transfer states have also been suggested to be precursors for excimer formation, however there is no compelling evidence.

Recently, it has become possible to use a supersonic beam to prepare cold, isolated dimers and higher clusters of species that were previously known to form strong excimers or exciplexes (excited state complexes between 2 different types of molecule) in solution. Saigusa and Itoh[2,3,4] first reported observation of exciplexes between the electron donor

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[2] H. Saigusa and M. Itoh, Chem. Phys. Lett. 106, 391 (1984).

[3] H. Saigusa and M. Itoh, J. Chem. Phys. 81, 5682, (1984).

[4] H. Saigusa and M. Itoh, M. Baba, and I. Hanazaki, J. Chem. Phys. 86, 2588 (1987).

triethylamine and the acceptor cyanonaphthalene which were formed in a supersonic beam. Following that work Saigusa et al. reported on an interesting series of exciplexes and excimers, involving aromatic hydrocarbons[5,6]. This work confirms that exciplexes and excimers are stable without solvation. (Although the fluorescence results do not rule out a requirement for noble gas solvation.) Overall, the low temperature gas phase results are quite similar to the earlier solution observations. However, high resolution gas phase spectroscopy promises to elucidate the nature of the intermolecular interactions in these species.

Saigusa, Itoh, Lim, and coworkers published work on fluorene dimer spectra measured in a cold supersonic beam using fluorescence detection. They observed red shifted fluorescence emission, which was drastically different from the fluorescence excitation spectrum. They attributed their spectrum to the dimer, as opposed to larger clusters, which might otherwise be expected to account for greatly red shifted emission. Recently, they have observed excimer emission from naphthalene trimer and tetramer clusters. Thus, it is becoming evident that excimer formation is a relatively general phenomenon for aromatic clusters. Excimer formation in these species is somewhat perplexing, because the excitonic interactions associated with the first excited states of the monomers appear to be insufficient to account for excimer formation. Understanding of this issue is of general scientific importance because the excimer interaction is involved in photodimerization a process that occurs in photobiology, including DNA degradation.

RESULTS AND DISCUSSION

The fluorene dimer spectrum was acquired by photoionization spectroscopy, in which the signal is obtained by monitoring the corresponding ion mass peak (mixed isotope dimer) Figure 1b , or by fluorescence excitation spectroscopy (isotopically pure dimer) Figure 1a, in which the red shifted excimer emission is monitored while the exciting laser frequency is scanned over the absorption spectrum. In the case of the isotopically pure dimer, the photoionization and fluorescence excitation spectra were substantially different, with a large broad baseline component accounting for much of the photoionization intensity. The cooling conditions were nominally similar for these two experiments, however the molecular beam skimmer was removed for fluorescence excitation spectra. It was not clear whether the two types of spectra are fundamentally different, or if the skimmer heats the beam in the photoionization experiments. It is important to know if the two types of spectra are fundamentally different because this could reveal details about the

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[5] H. Saigusa and M. Itoh, J. Phys. Chem 89, 5486 (1985).
[6] H. Saigusa and M. Itoh, J. Phys. Chem 94, 2631 (1990).

ionization and excimer formation processes. Therefore, extensive efforts were made to resolve this problem. Photoionization experiments were performed without a skimmer, and the results were close to those obtained with a skimmer. Apparently the ion detection grid structures perturbed the beam in this case. New skimmers of high quality were employed. For short periods of time, given very delicate control of pulse expansion conditions, segments of spectra displayed improved sharpness. This suggested that the system operated on the threshold of turbulent flow, in which the beam can interact with, and be heated by, the skimmer and ion acceleration grids. In order to resolve this problem, the entire molecular beam system was rebuilt, increasing the distance between the pulsed nozzle and the skimmer, and by greatly increasing the size and smoothness of the skimmer assembly, so that spurious beam reflections from surfaces could not interfere. These modifications made it possible achieve cooling in the photoionization spectra approaching that obtained using fluorescence detection. It appears to be converging to the best fluorescence detected spectrum (Figure 1a), however it is still not clear if the additional baseline seen in photoionization is due to incomplete cooling.

For the purposes of this report, we assume the differences between photoionization and fluorescence detection are caused by incomplete cooling, and the spectrum consists of a number of discrete components that span the monomer origin transition. Previously, we studied the intramolecular vibrations of the fluorene dimer (Figure 2) and concluded that excitonic interactions are greatly suppressed for these transitions. The origin region spectrum is unique, and appears to be highly irregular in structure, thus defying simple conventional analysis.

The key to interpretation of the spectrum was provided by the mixed isotopic dimer species in which one fluorene molecule is fully protonated and the other is fully deuterated. It was essential to be able to obtain cold photoionization spectra in order to measure the mixed dimer spectrum because the molecular beam contains a mixture of pure and mixed dimers when the feed gas contains both isotopes of the monomer. Thus, mass spectrometry must be used to separate the mixed isotope signal. The electronic origin of the deuterated monomer occurs at a transition energy 109 cm^{-1} higher than for the protonated monomer. Thus, the resonance condition is broken for the mixed isotope dimer, thereby suppressing the excitonic splitting. The origin transition of the dimer, corresponding to the protonated molecule, occurs at lowest energy. It is expected to be near the unsplit (zero order) position for the pure protonated dimer. As shown in Figure 1a, the origin components for the pure protonated dimer are separated into two groups, one below the mixed isotope origin (33560 to 33580 cm^{-1}), and another group above this position (33580 to 33610 cm^{-1}). We believe that these two groups represent the lower and upper intermolecular potential surfaces, corresponding to the two excitonic components.

The mixed isotope spectrum provides information on the unperturbed intermolecular vibrational frequencies. Two vibrations are active, one at $+5\ \mathrm{cm}^{-1}$ and another at $+14\ \mathrm{cm}^{-1}$. The $+5\ \mathrm{cm}^{-1}$ vibration may contribute to an overtone with weak intensity on the low energy shoulder of $+14\ \mathrm{cm}^{-1}$. The $+5\ \mathrm{cm}^{-1}$ feature has predominant intensity, therefore it is expected to dominate in modulating the excitonic interaction. The observed intensity distribution is best fit by a harmonic oscillator displacement coordinate $Q = 1.7$. (The low frequency of this mode suggests that it may involve complex motion, and thus be described by an anharmonic potential. In this case, it is not clear that the mixed isotope origin will be midway between excitonic components. In the analyses below, we do not treat this offset, nor the absolute difference between the two potential surfaces.)

The treatment employed here is similar to that used to analyze Jahn-Teller interactions in symmetric molecules. Namely, the full electronic Hamiltonian generates displaced adiabatic potential surfaces corresponding to the two excitonic states. Intermolecular motion occurs on these surfaces, and any deviations from Born-Oppenheimer behavior are induced by off-diagnoal elements of the nuclear kinetic energy operator. Calculations of the energy spectrum were performed using an extensive set of diabatic harmonic oscillator wavefunctions, centered at the ground state configuration. A displacement parameter was introduced for a single excited state potential surface, and matrix elements were calculated, including terms up to quartic in displacement along the intermolecular normal coordinate. (Linear plus quadratic terms are generally adequate for the Jahn-Teller problem.) Diagonalization provided energies and overlap functions $S(1,i)^2$ for intensities. The interaction matrix elements were adjusted iteratively, until the positions and intensities observed in the lower branch were predicted correctly.

Results are shown in Figure 3. The lower potential surface was found to be dominated by the quartic term, with a small negative quadratic contribution. Both these potentials were centered about an equilibrium position displaced by an amount $Q = 1.7$, from the ground state potential, which is the same as that deduced independently from the mixed isotope spectrum. This implies that the excitonic interactions are not important in determining excited state geometry.

The analysis indicates the potential surfaces are separated by $20\ \mathrm{cm}^{-1}$, which implies that the electronic interaction matrix element is $10\ \mathrm{cm}^{-1}$. The coupled intermolecular coordinate has an unperturbed frequency of $5\ \mathrm{cm}^{-1}$. Therefore, the system is characterized by the strong coupling limit. Overall, there is excellent agreement between the adiabatic model and the observed spectra. The most surprising outcome is the need to invoke high order (quartic) coupling.

The above considerations apply to the lower adiabatic potential surface. In the excitonic model, the upper potential surface can be related to the lower one by reflecting the perturbation potential upward. That is, for the dimer, the unperturbed surface is split symmetrically upward and downward by the excitonic interaction. However, the quartic perturbation potential is not meaningful for the upper surface because it makes the upper surface asymptotically unbound. However, as indicated by Figure 3, which is scaled to represent the optimum lower surface, for short displacements, the quartically perturbed upper surface remains close to parabolic, although the lower surface is largely quartic. Thus, the upper surface can be fit, to good approximation, by a stiffer **harmonic** potential. The required force constant for the upper surface is 1.4 times that for the unperturbed harmonic surface. Thus, the upper surface vibrational progression is projected to have a frequency of $\sqrt{1.4} \bullet 5$ cm^{-1}, which is close to the observed 7 cm^{-1}. It is not surprising that the second overtone appears to be significantly split, because anharmonic effects should increase rapidly with quantum number. Considering that the truncated power series expansion in the perturbation potential probably provides a poor representation of the interactions, it is not surprising that predicted intensities are somewhat inaccurate. However, it should be noted, that if a more realistic potential fails to predict the observed intensities, the discrepancy points to an inadequate treatment of Born-Oppenheimer breakdown (i.e. off-diagonal terms in nuclear kinetic energy are required).

The presumed second intermolecular mode at 12 cm^{-1} should be mentioned. This mode will be much less effective in modulating excitonic coupling than the 5 cm^{-1} mode, due to the smaller Franck-Condon factor. Therefore, in the pure isotope dimer spectrum, the mode should be unshifted in energy and have weak intensity. The weak feature at 33578 cm^{-1} in the pure isotope spectrum may represent this mode. Failure to include this mode in the Hamiltonian may also compromise the accuracy of the calculations.

An alternative interpretation can be given to the mixed dimer origin spectrum. Whereas, the mixed isotope intermolecular potential surface was assumed to be harmonic, with two active intermolecular modes, it is also possible that the dimer spectrum has a single, highly anharmonic, optically active intermolecular mode. In this case, the analytical model would be inaccurate. The success of the model argues against this possibility.

In conclusion, this work provides a nearly complete qualitative and adequate quantitative description of excitonic interaction in the first singlet state of the fluorene dimer. It demonstrates that excitonic interactions generate effective adiabatic intermolecular potential surfaces in the strong coupling case. This permits separation of intermolecular and electronic coordinates. This spectrum does not show obvious evidence of non-adiabatic effects nor does it show direct evidence of excimer forming interactions.

FUTURE PLANS

After the fluorene dimer problem is resolved, we intend to investigate the fluorene trimer. We have extensive low resolution spectra for this species, however high resolution mixed isotope spectra for ultracold clusters will be needed in order to reach definitive conclusions about trimer structure. As in the case of naphthalene, it is likely that the geometries of the small fluorene clusters are highly dependent on the size. This is an issue of considerable significance because it depends on the intermolecular force field.

Following these direct spectroscopic investigations, we intend to use cluster fragmentation spectroscopy in order to determine cluster geometries. This approach is described in the accompanying continuation proposal.

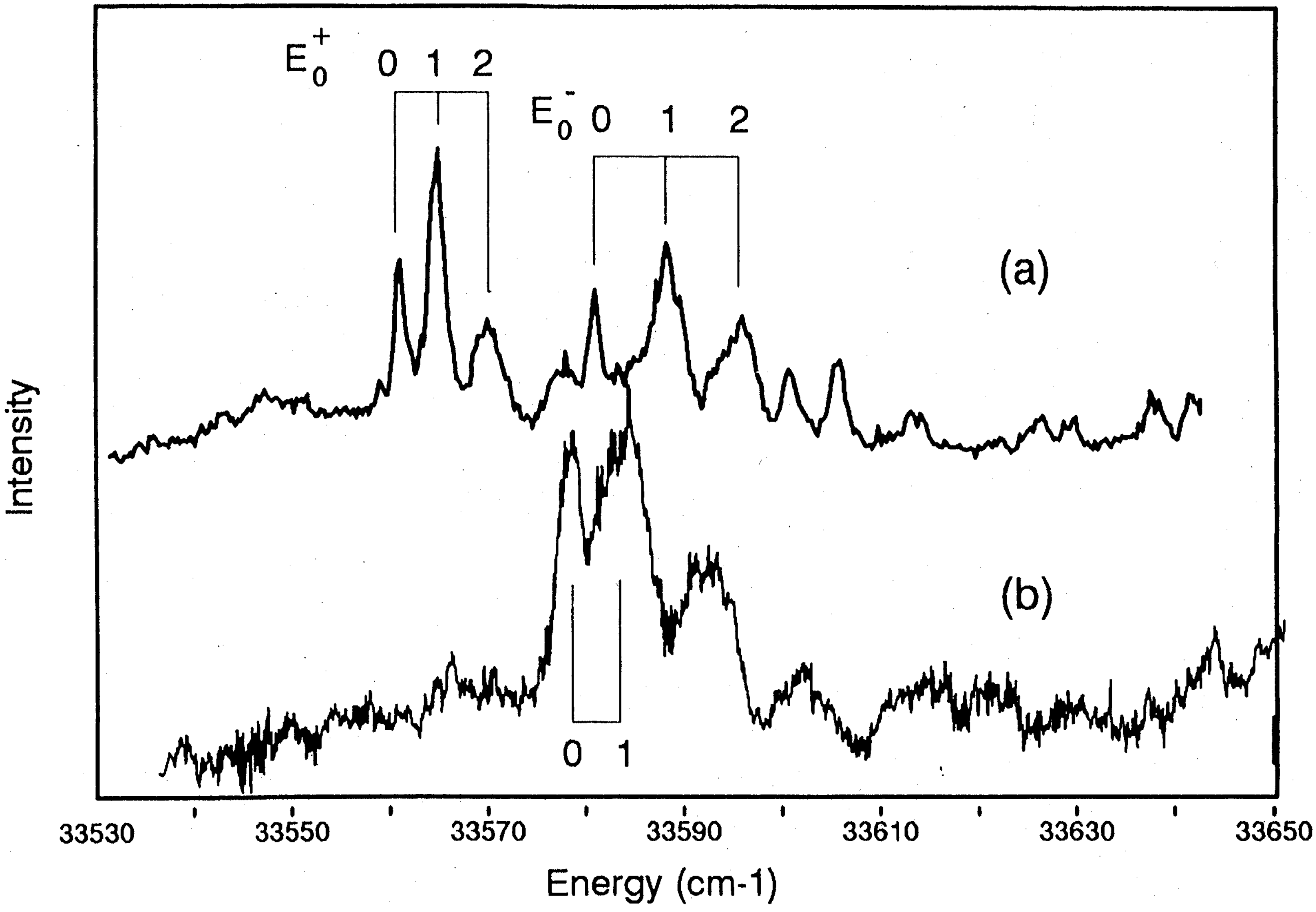
Figure Captions

1. Origin region of the fluorene dimer S_1--S_0 spectrum. (a) isotopically pure dimer, recorded by fluorescence excitation, (b) mixed isotope dimer ($C_{13}H_{12}$-$C_{13}D_{12}$) measured by photoionization spectroscopy with mass selective detection.

2. Origin and excited vibrational levels of the dimer S_1--S_0 spectrum of isotopically pure fluorene recorded by photoionization. Cooling was incomplete for this spectrum.

3. (a) Observed and (b) calculated origin region spectra for the isotopically pure fluorene dimer. The full lines represent the lower potential surface, and the broken lines are for the upper surface. For the calculated spectrum, the linear displacement parameter was 1.7, the quartic coupling constant was 0.05 * 5 cm^{-1}, the quadratic correction was -0.05 * 5 cm^{-1}, and the offset between the lower and upper potential surfaces was arbitrarily set at 20 cm^{-1}. The upper potential surface was assumed to be harmonic with a force constant equal to 1.4 times that for the principal intermolecular vibrational mode of the mixed isotope dimer.

4. Intermolecular potential curves for the fluorene dimer. (a) is the ground state potential, which has been scaled to unit energy for one quantum in the principal mode (5 cm^{-1}) and where Q is the harmonic oscillator displacement coordinate. The offset between the ground state (a) and the excited states (b)--(e) is arbitrary. Curve (c) represents the unperturbed (harmonic) dimer excited state, (b) is the perturbed lower potential surface (quartic constant 0.05, quadratic constant -0.05), (d) is part of the correspondingly perturbed upper surface, and (e) is a harmonic approximation to the perturbed upper surface. The excitonic splitting at Q = 1.7 has not been included in these potentials (b)--(e).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1
2
E_0^-
0
1
2
(a)
(b)
0
1
Intensity
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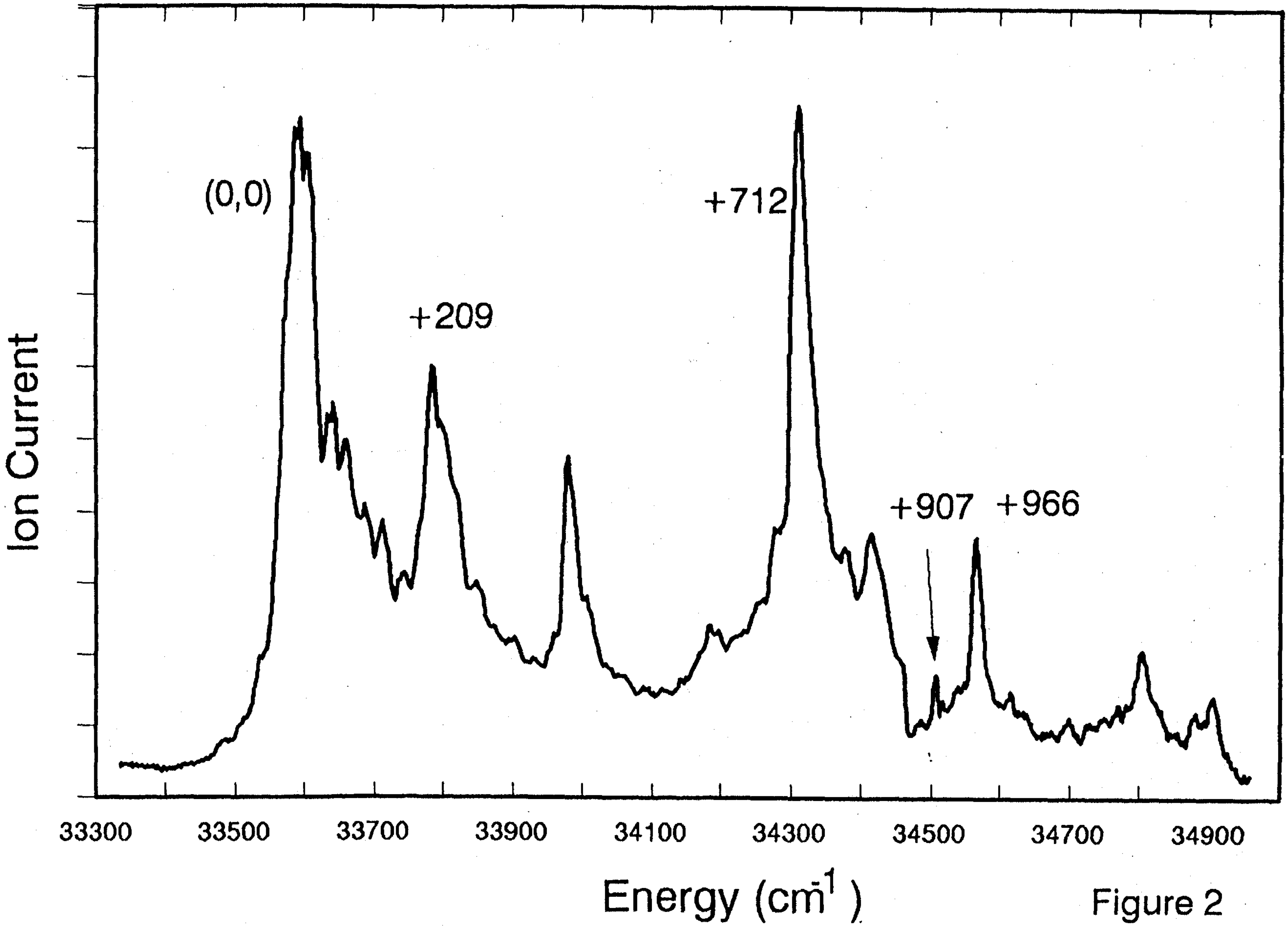
33550
33570
33590
33610
33630
33650
Energy (cm-1)

Figure 1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+907
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Ion Current
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33500
33700
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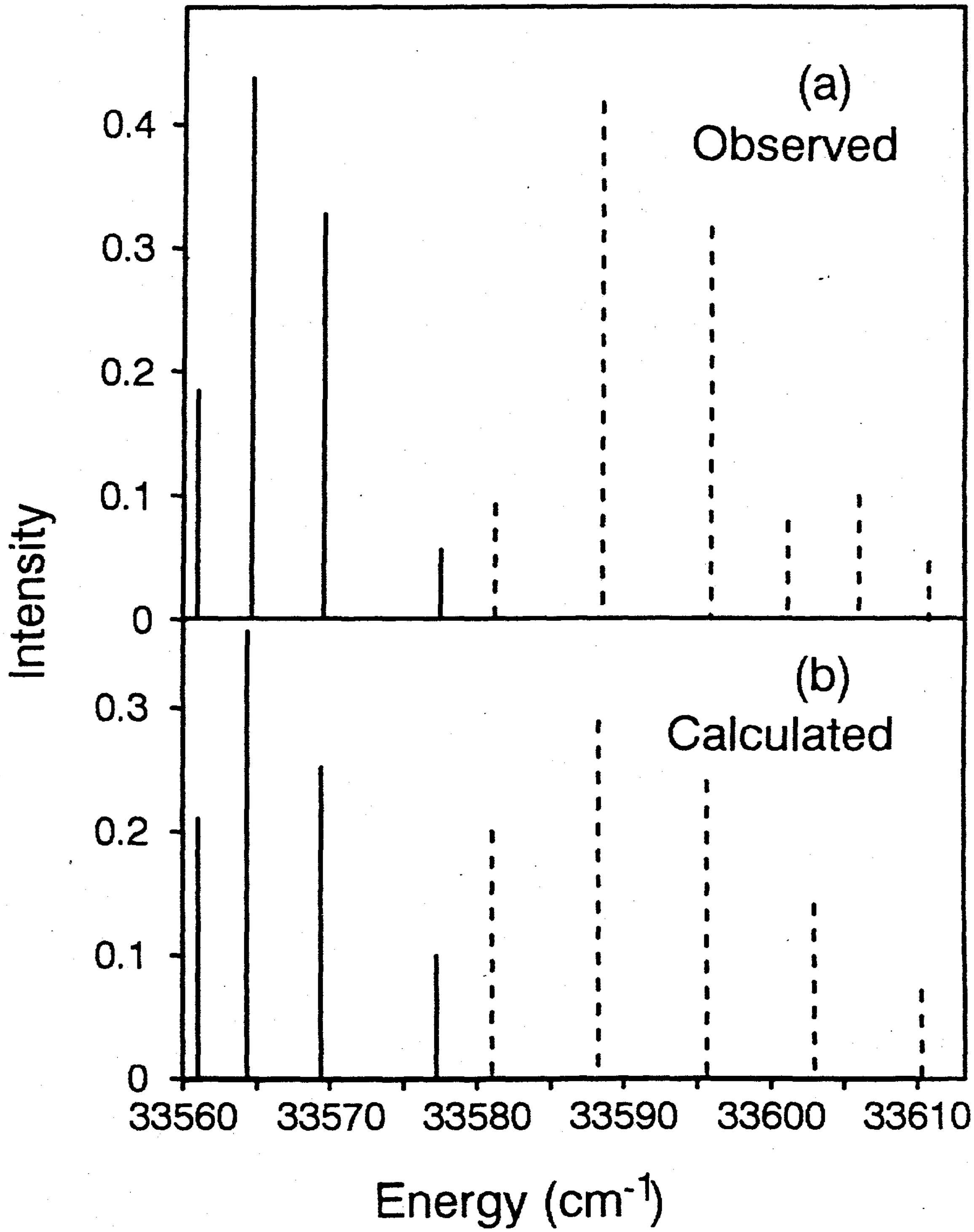
34100
34300
34500
34700
34900
Energy (cm^{-1})

Figure 2


(a)
Observed
(b)
Calculated
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0.3
0.2
0.1
0
0.3
0.2
0.1
0
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33570
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33590
33600
33610
Energy (cm^{-1})

Figure 3

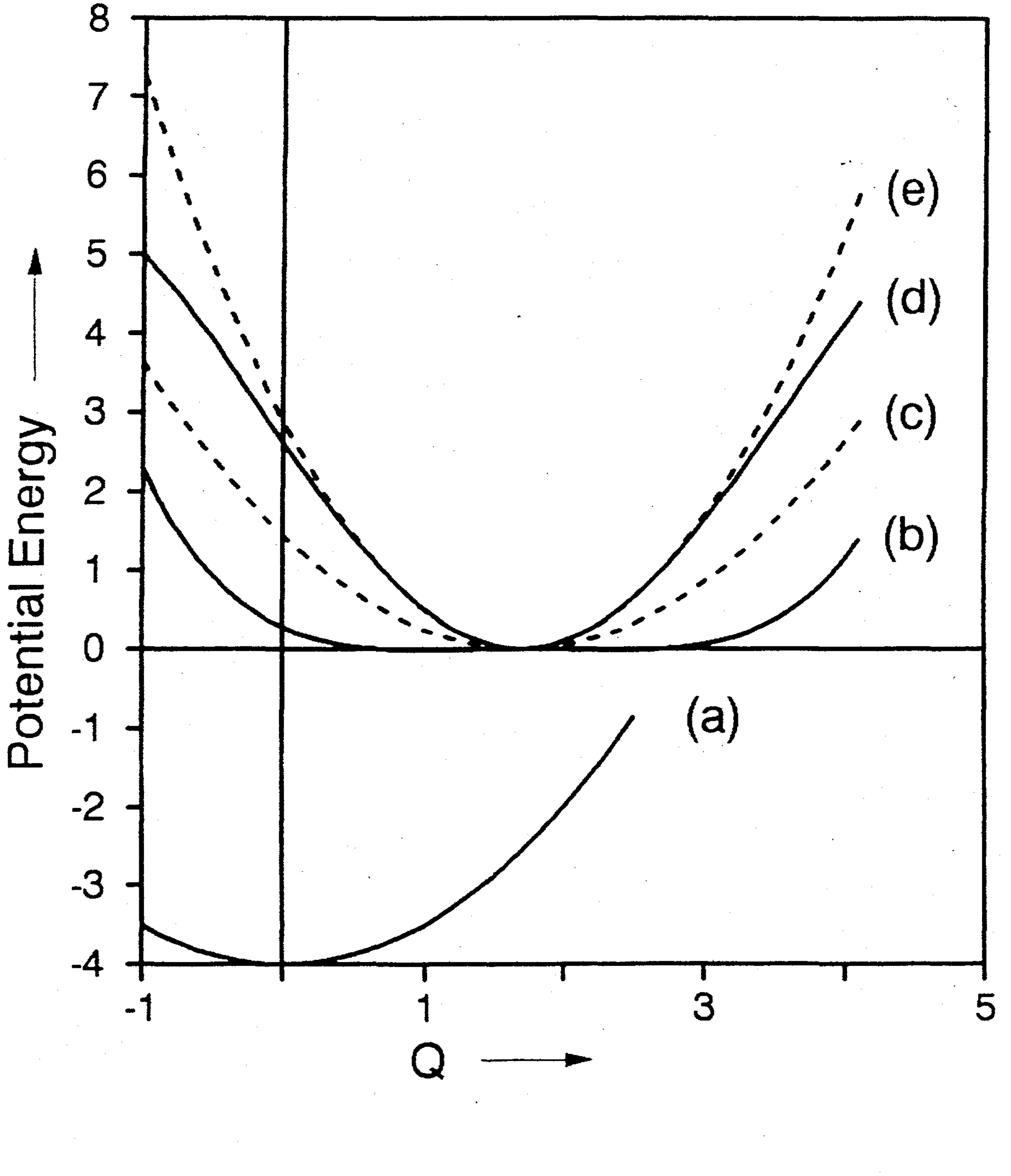

Figure 4