Vibrational Predissociation and Dimer Spectroscopy

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Since 1978, the experimental technique introduced by Giacinto Scoles and his colleagues in Waterloo, infrared spectroscopy of dimers formed in the supersonic expansion of a molecular beam, has produced much information on the interaction between vibrationally excited molecules. If the applied laser is given the right frequency, constituents of molecular complexes become excited and the complexes themselves are destroyed by predissociation before reaching the molecular beam detector (see Fig. 1).

Supersonic Beams and Cluster Production

The technique of supersonic expansion of molecular beams already described (see p. 12) has won wide acceptance as a means of obtaining wanted species in energetically low lying states. To obtain rotational temperatures of about 1 K is no longer considered to be a difficult task.

Not surprisingly in a medium of such low temperatures, complexes bonded by van der Waals forces are formed and because of the absence of collisions remain stable down-stream of their zone of genesis. Becker, Hagena, Gespann and others of the Karlsruhe group claim rightly to have been the first to observe even very big clusters and to have introduced new techniques for their investigation (coping with units of tens of thousands of atoms). Dimers are the smallest members of this complex family. They can consist of two equal constituents, e.g. Ar_2, or of combinations like O_2-He, produced in seeded beams, i.e. a He expansion, seeded by an admixture of typically 1% (often less) of O_2.

The mass spectrometric detection of clusters is difficult owing to their tendency to fragmentation upon ionisation and one of the few ways of distinguishing between neutral dimers and daughter cluster ions, is by spectroscopy utilizing IR predissociation.

ATOMIC and MOLECULAR PUBLICATIONS

BOOKS AND JOURNALS

Electronic and Atomic Collisions

(Proc. of the XIV Int. Conf. on the Physics of Electronic and Atomic Collisions, Stanford Univ., 24-31 July 1985)

Lorents, D. C., W. E. Meyerhof and J. R. Peterson *(editors)*

1986
In preparation

As of 1979 (KYOTO, Japan, 29 Aug.–4 Sept.,) the proceedings of the ICPEAC conferences have been published by North-Holland. All of these proc. are still available.

Molecular Ions: Spectroscopy, Structure, and Chemistry

Miller, T. A. and V. E. Bondybey *(editors)*

1983 xii + 278 p.
US $ 53.25/Dfl. 125.00
ISBN 0-444-86717-1

For many years the rich chemistry and physics of molecular ions were the almost exclusive domain of mass spectroscopists. While mass spectroscopy and related techniques can give very useful data about the existence and stability of molecular ions, they provide little information about their structures and usually cannot even differentiate between isomeric species. Recently a variety of other, structurally more sensitive experimental methods have been applied to the study of molecular ions. Most of these techniques involve absorption or emission of photons and fall into the general area of spectroscopy. Application of these techniques has yielded a wealth of new information about molecular ions, their geometry, their electronic structures and their chemistry. This book contains contributions from many of the most important persons connected with this advance.

Handbook on Synchrotron Radiation, Vol. 1

(Characteristics, Instrumentation and Principles of Research Applications)

Koch, E.-E. *(editor)*

Part A

1983 lxvi + 606 p.
US $ 149.00/Dfl. 350.00
ISBN 0-444-86709-0

Part B
1983 lxvi + 560 p.
US $ 149.00/Dfl. 350.00
ISBN 0-444-86710-4
Set price
US $ 255.25/Dfl. 600.00
ISBN 0-444-86425-3

This first volume deals with the characteristics of synchrotron radiation, with instrumentation and research applications providing a maximum of useful information in graphical and tabular form. The topics, covered in up-to-date review form by well-known specialists, are presented on a tutorial level.

In Preparation:

Volume 2

edited by G. V. MARR, *Aberdeen University, Aberdeen, U.K.*

New Trends in Atomic Physics

Grynberg, G. and R. Stora *(editors)*

(Les Houches Summer School Proceedings, 38)

Vol. I 1984 xxviii + 564 p.
US $ 133.25/Dfl. 360.00
ISBN 0-444-86908-3

Vol. II 1984 xxvi + 686 p.
US $ 157.50/Dfl. 425.00
ISBN 0-444-86908-5
Set price US $ 259.25/Dfl. 700.00

The purpose of this Les Houches Summer School was to present some classical topics of Atomic Physics and discuss them in terms of their future development, and secondly, to consider other domains of physics where the methods or techniques used within Atomic Physics could be applied within the foreseeable future.

Gas Phase Chemiluminescence and Chemi-Ionization

Proc. of a Symp.

Fontijn, A. *(editor)*

1985
In preparation

In recent years there have been a large number of interesting developments in the areas of gas-phase chemiluminescence and chemi-ionization. The aim of this symposium was to collect in one place a report on these developments and to point the way for further research.

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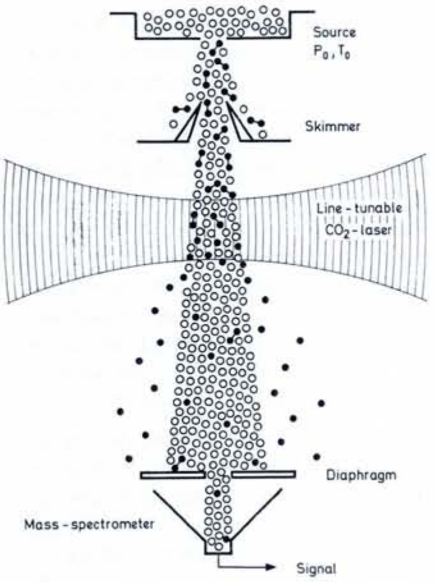

Fig. 1 — Typical molecular beam set-up for the study of dimer spectroscopy employing a CO_2 laser.

IR Predissociation of Dimers: Life-time

If a dimer absorbs an energy quantum of 0.12 eV corresponding to the absorption of a single CO_2 laser photon (about 1000 cm^{-1}), it typically climbs into a state very much above the dissociation threshold for a van der Waals complex. Nevertheless, it does not fly apart immediately, since some time is needed to redistribute the energy "intermolecularly". How long this time really is has not been demonstrated yet, but it is expected to be rather long because of the big mismatch between the initially excited mode (1000 cm^{-1}) and the final dissociative van der Waals stretch mode ($\cong$ 20 cm^{-1}). One expects also very large variations: H_2-Ar with its extreme mismatch is expected to live much longer than CF_3Br-Ar, where many in-between levels are avalable to facilitate the energy repartitioning.

Experimentally, the situation is really undetermined. With a few exceptions, the observed linewidths are all about 10 cm^{-1} fwhm, yielding a lower limit for the life-time of the predissociation state of about 0.5 ps. The upper limit is set by the time of flight between excitation zone and molecular beam detector; if the excited complex can survive that distance the beam signal is not attenuated. Typical beam velocities are 500 m/s, typical laser detector distances 0.5 m, thus yielding 1 ms as upper limit.

Recently, Hoffbauer, Giese and Gentry (Minneapolis, USA) proposed that the linewidth might change drastically if one could predissociate a complex by a CO_2 laser photon whose energy was barely sufficient to reach the dissociation threshold. Taking the hydrogen bonded system $(CH_3OH)_2$, they found that indeed the product velocities in the centre of mass system became very low (50 m/s), but detected no change at all in the fwhm linewidth. They argued that the 0.4 ps minimum lifetime (deduced from the linewidth) would be just long enough for the dissociation products to move apart about 0.2 Å. They concluded therefore that the linewidth cannot reflect the lifetime of a complex with respect to dissociation but forms a measure of the typical time of energy redistribution within the complex.

Line Shifts

Whilst the linewidth failed to give the information sought, the line shift starts to do so. Intuitively one expects a small red shift from the following argument. Consider the vibrational ground state of a molecule that forms part of a dimer. Above this there exist many close lying states from van der Waals stretch vibrations or orientational vibrations, which interact slightly with the internal motion of the considered molecule. This leads to level repulsion, i.e. a lowering of energy of the ground state. Similarly if we take the first excited molecular state which, on one side, is bordered by a manifold of van der Waals vibration states, its energy is again lowered. But as the amplitude of the motion is larger for the first excited state, the interaction with the nearby states is bigger than for the ground state, and the distance between ground state and first excited state is consequently decreased, leading to a red shift.

In practice, however, as many blue shifts as red shifts are observed, at least for polyatomic molecules and the inference is drawn that Fermi-resonances ("switched on and off") play a vital role in producing the observed shifts. Take the CO_2 molecule, where Fermi discovered "his" resonance. The first ν_1 mode is nearly degenerate with the $2\nu_2$ level, both possessing the same symmetry. Thus mutual interaction leads again to repulsion. However, if the CO_2 molecule is accompanied by an Ar atom (as in the dimer CO_2-Ar) the symmetry is perturbed and the very strong Fermi-resonance is weakened. This is precisely what has been observed — and in other molecules too, notably the related OCS molecule. The shift caused by attenuation of a Fermi-resonance can be quite substantial, i.e. up to 10 cm^{-1}.

Yet the contrary can also happen. Take the ν_7 mode of C_2H_4 (a butterfly mode, as both H_2-ends perform an in-phase out-of-plane motion); this mode is nearly degenerate with the ν_8 mode (here the H_2-ends perform the same motion, but 180^0 out of phase). There is one subtle difference between this and Fermi's CO_2 case; ν_7 and ν_8 possess different symmetries and cannot interact in the monomer. If, however, these symmetries become slightly perturbed, as in a dimer, they start to interact producing a level repulsion. This can explain the observed blue shift in the ν_7-absorption of $(C_2H_4)_2$.

The reasoning seems to work although it becomes ambiguous for very large molecules with many low-lying modes. There one can produce blue and red shifts at will, since many nearby levels offer their help.

The Sum Rule

If the sum rule is applied to dimers it says that the total integrated low power absorption strength has to be conserved if integrated over the small frequency band $\triangle\nu$, wherein shifts and broadenings take place (typically 30 cm^{-1}). The assumption is that no order modes are active within the bandwidth $\triangle\nu$. Phrased in this way the statement is nearly tautological: if one does not "export" absorption strength from $\triangle\nu$ elsewhere and if one does not "import" absorption strength from elsewhere into $\triangle\nu$, the absorption strength should remain constant. Consequently $(SF_6)_2$ e.g. should absorb twice as much around 948 cm^{-1} as SF_6, $(SF_6)_{10}$ ten times as much and so on.

Not everybody is happy with this rule, e.g. R.P. Watts, R.F. Miller and coworkers (Canberra, Australia) seem often to observe a stronger enhancement for dimer absorption than the sum rule permits. The simplest explanation for this deviation holds the polarizability of the dimer partner to be responsible for an induced time-dependent dipole moment. This oscillates with the frequency of the transition dipole moment and leads to an enhancement of absorption strength in one band and a decrease in another. But there can be more; consider a dimer partner with a strong permanent dipole moment which induces in the other partner a moment that is time-independent by virtue of its polarizability. If, moreover, the distance between the two dimer partners starts to vary slightly with the mode-frequency absorbed (remember, both sit in the potential well which is a compromise between attractive and repulsive forces), then the DC-induced dipole moment also acquires a time-dependent component which may be larger than that directly induced as discussed above (the ratio amounts to $(3\mu\triangle R)/(R\mu_{01})$ where μ is the DC-dipole moment, μ_{01} the transition dipole moment, R the dimer distance and $\triangle R$ its variation in synchrony with the mode-oscillation). $(H_2O)_2$ is a good example of a dimer of small R (H-bonding) and large μ; moreover the mode-amplitudes of H-atoms are relatively large, producing sizable $\triangle R$ variations. The general conclusion is that the larger the deviation from the simple sum rule, the more perturbed the dimer constituents are by their mutual presence, resulting in import and export of transition strength.

The Exceptions

There are two exceptions to the large linewidth normally observed. The first is the group of hydrogen-noble gas dimers, which have been measured in an absorption multiple pass cell at low temperatures and high pressures. On top of the broad pressure-induced absorption band, McKellar and co-workers (Ottawa, Canada) have revealed with ever-increasing accuracy, sharp structures (0.1 cm^{-1} fwhm). Analysis of these spectra by R.B. LeRoy and co-workers (Waterloo, Canada) indicates a connection between linewidth and lifetime.

Further, in IR predissociation measurements, Janda and co-workers (Pasadena, USA) have found that C_2H_4-Ne, and to a lesser extent also C_2H_4-Ar, exhibit a fine structure (0.5 cm^{-1} fwhm) which is tentatively attributed to internal motions of the dimer system. To achieve this, extreme expansion cooling was applied, in a 0.5% C_2H_4, 10% He and 85.5% Ne mixture which opens the door to a new field of dimer dynamics in the 500 GHz region, a field one could glimpse only indirectly, up to now, using the powerful molecular beam electric resonance technique pioneered by Klemperer and others (Harvard, USA).

Another example of the second group of exceptions is $(SF_6)_2$, in which J. Geraedts (Nijmegen, Netherlands) has observed a double peak structure (spacing 20 cm^{-1}, fwhm linewidth 1.5 cm^{-1}) attributed to resonance dipole-dipole forces. The blue peak arises from a vertical transition, the red from a parallel. These can be exploited to dissociate preferentially certain orientations of the dimer axis, to study orientational hole burning effects in detail and to test the sum rule for a non-trivial case. Extending the technique to the measurement of spectra of larger clusters at higher source pressure, extra features appear.

Within the past few months quite remarkable results have been announced. Miller and Watts (Australia) have found dimer linewidths on $(C_2H_2)_2$,

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$(CO_2)_2$ and $(N_2O)_2$ as small as 3 MHz, yielding an upper limit of 50 ns for the lifetime of the upper state. Simultaneously, DeLeon and Muenter have measured vibrationally excited $(HF)_2$ dimers and found comparable linewidths. The door is thus now wide open for the determination of dimer structures and intra-dimer dynamics.

Applications

Dimer predissociation can be achieved with the absorption of a single photon. If there are big differences between the spectra of molecules of different isotopic composition, the method would hold promise for applications in the future. The group of Manot and van den Bergh (Lausanne) who have been pursuing this line have recently come up with an elegant two-stage scheme. We discuss it by considering SF_6 which can be considered to have two isotopomers ($^{32}S\ ^{19}F_6$ and $^{34}S\ ^{19}F_6$). First, the 0.5% SF_6 in Ar mixture is irradiated close to the nozzle (see Fig. 1) so that one monomeric isotopomer becomes excited and is inhibited from forming clusters (*i.e.* SF_6-Ar_n). Then, a second laser downstream predissociates those clusters that have been formed, and the fragments collected contain only the other isotopomer. Note that the first laser is tuned to induce absorption of a photon by one monomer, which possesses narrow and well defined absorption bands. On the other hand, the second laser does not need to distinguish separate absorption bands for different isotopomer dimers; only one type is present due to the inhibition of the formation of the other by the first laser. The great advantage of the Lausanne method is that only one (single expensive) IR photon is needed per molecule to achieve enrichment (in contrast to the MPD schemes). Another application stems from the unique possibility of being able to identify and select certain dimers by their spectra (e.g. $(SF_6)_2$ and C_2H_4-Ne, the exceptional cases). By tuning the mass spectrometer detector to different masses, the fragmentation has been determined quantitatively. For $(SF_6)_2$ it has been found by the Nijmegen group that the dimers show up on the mass of SF_5^+ at least a hundred times more frequently than on the dimer ion mass SF_6-SF_5^+.

Further Reading

Attention is drawn to two comprehensive articles:

Gentry W.R., "Vibrationally Excited States of Polyatomic van der Waals Molecules: Lifetimes and Decay Mechanisms", *ACS Symposium Series* **263** (1984) 289-303.

Janda K.C., "Predissociation of Polyatomic van der Waals Molecules", *Adv. Chem. Phys.* **60** (1985) in print.

Atomic Processes in Astronomy

M.J. Seaton, London

(University College)

The astronomer is often concerned with the behaviour of matter under conditions which are unusual from the standpoint of the laboratory physicist, either because they are very simple or because they are very extreme. In either case, studies of such conditions have led to important advances in basic physics. Many examples could be given: studies of the laws of dynamics and gravitation, of ultra-high densities, and of thermonuclear energy generation. I consider some examples from atomic physics.

Many astronomical spectra differ from laboratory spectra as a consequence of being produced at very low densities (the pressure in a typical gaseous nebula is of order 10^{-14} atm, that in the interstellar medium about 10^{-20} atm) and this simplifies their interpretation. The way in which strengths of lines depend on density can be understood by considering carbon-like ions, which have ground configurations $1s^2 2s^2 2p^2$ with three terms, ^3P, ^1D and ^1S. The energy-level diagram for the carbon-like ion O^{2+}, which gives strong lines in many astronomical spectra, is shown in Fig. 1. Since the ground configuration terms all have the same parity, radiative transitions between them cannot occur by electric-dipole radiation. Such levels are said to be "metastable" and the transitions to be "forbidden", but they can take place by electric-quadrupole or magnetic-dipole radiation with probabilities of the order of 1 s^{-1} compared with 10^9 s^{-1} for "allowed" lines. In radiation from laboratory sources the forbidden lines are very weak, and are rarely seen, but in the spectra of gaseous nebulae they are often the strongest features observed. The number of photons emitted per unit time in a transition 2 → 1 is given, in all cases, by

$$P_{21} = N_2 A_{21} \tag{1}$$

where N_2 is the number of atoms in the upper level and A_{21} the radiative transition probability. At densities of laboratory sources, the probabilities of transitions due to collisions are much larger than $A_{21} \cong 1 s^{-1}$. To a good approximation, the relative populations of the ground and metastable levels are given by the Boltzmann equation, and the forbidden lines are very weak, compared with other lines, because A_{21} in (1) is very small. At the low densities of nebulae, collisions are much less frequent and are mainly due to electron impacts, which produce both excitation and de-excitation. Let N_e be the electron density and $q_{ij} N_e$ the probability of a collisional $i \rightarrow j$ transition ($q_{ij} = \langle v_i Q_{ij} \rangle$ where v_i is the velocity of the incident electron, Q_{ij} the collision cross-section, and the average is over the velocity distribution). At a critical density $N_e(c)$, such that $q_{21} N_e(c) = A_{21}$, the probability for collisional de-excitation equals that for de-excitation by emission of radiation. For the forbidden lines, typical values of $N_e(c)$ are of order $10^4\ cm^{-3}$. For $N_e << N_e(c)$ effectively every excitation by electron impact is followed by emission of radiation, giving

$$P_{21} = N_1 q_{12} N_e \tag{2}$$

which is independent of A_{21}. Densities $N_e \leq N_e(c)$ frequently occur in gaseous nebulae and this explains why the forbidden lines can be the strongest features in their spectra.

The observed spectra provide the astronomer's only means of estimating temperatures and densities in nebulae. If the condition $N_e << N_e(c)$ can be assumed for two lines (such as the λ = 5007 Å and 4363 Å lines of Fig. 1), the ratio of their intensities will depend only on the ratio of their excitation rates, and

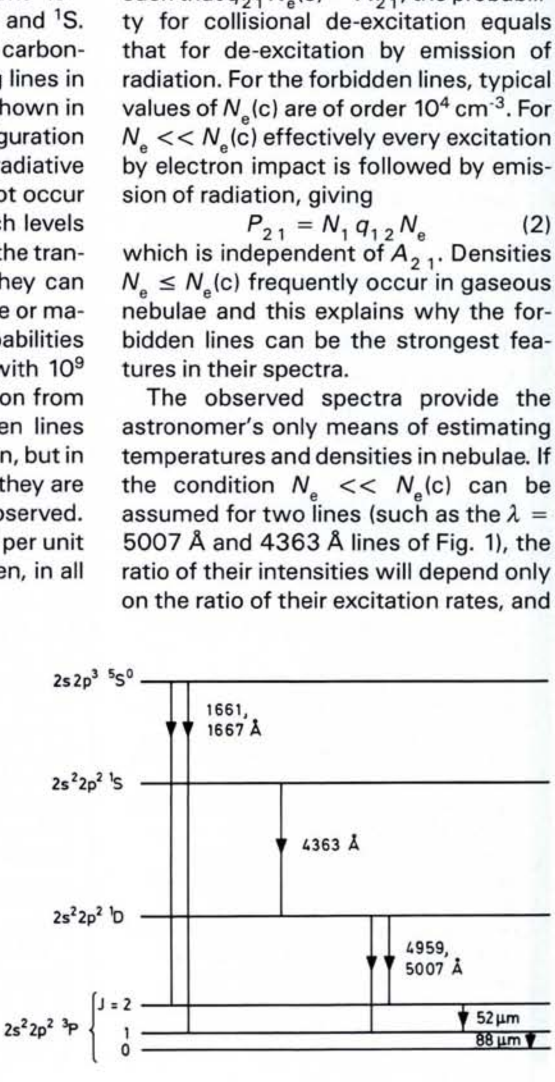

Fig. 1 — Partial energy-level diagram for O^{2+} (not to scale) showing lines observed in the spectra of nebulae at IR, optical and UV wavelengths.