

Molecular Negative Ion Structure

It has long been known from mass spectroscopy that a great many common neutral molecules are able to attach electrons to form negative ions. The neutral molecules have been the subject of an enormous amount of study by spectroscopic techniques. Their mechanical constants have been determined with great accuracy and duly enshrined in the literature, most notably in Herzberg's famous book *Spectra of Diatomic Molecules*.¹ Mechanical constants of the dual forms, the molecular negative ions, are not found there, or anywhere else until quite recently. They have remained largely shrouded in mystery. Properties have been inferred from considerations of molecular orbital theory, but the relevant experimental data have been so sparse as to be virtually nonexistent.

At the root of this situation, of course, is the fact that negative ions cannot be collected in sufficient density in a laboratory for optical absorption or emission to occur to a measurable extent. To the extent that they occur as populations in equilibrium with free electrons, neutral molecules, and positive ions, the low negative ion densities are easily explained in terms of the very small energy with which the extra electron is bound in most molecular negative ions. A similar situation has prevailed for atomic negative ions, although more recently absorption continua for several atomic negative ions, principally the relatively strongly bound halogen ions, have been observed² in electron seeded shocks.

The first spectroscopic method for systematically studying the structure of negative ions was developed by Branscomb *et al.*³ A version of absorption spectroscopy, it capitalized on the enormous sensitivity with which a current of free electrons can be detected. The "photodetachment" electron current was a measure of the photon absorption probability. However, with this technique very high photon fluxes are required, and, in pre-laser days, this meant very wide optical bandwidths, perhaps several hundred angstroms. For purposes of structure measurements the photoelectric threshold could often be determined quite accurately but the prospect for resolving other structural details was not bright. Therefore, the method was valuable for determining binding energies in atomic negative ions. However, for the

molecular case even the vertical detachment threshold energy does not provide unambiguous information because of the operation of the Franck-Condon Principle and the uncertainty of equilibrium internuclear distance r_e in the negative ion. It was plausible to interpret the steep threshold of photodetachment from OH^- as implying an equilibrium internuclear distance unchanged by the addition of an electron and an electron affinity EA equal to the observed threshold energy. The O_2^- photodetachment spectrum, however, dribbled off toward a zero level which was estimated to occur at about 0.15 eV. For lack of a better value 0.15 eV was widely used for some time for the electron affinity in aeronomic equilibrium calculations, giving way later to a determination (~ 0.43 eV) by Pack and Phelps⁶ based on studies of attachment in a drift tube. Lack of spectral resolution thwarted all further efforts to extract clues from the experimental data which might establish molecular constants and determine the energy of the negative ion ground state with respect to neutral molecule energy levels.

The needed spectral resolution has come along with the laser, and some very significant laser measurements have emerged in the past year or two which seem to presage an era of rapid development of data on the molecular negative ion constants.

The fixed frequency laser is, of course, of no immediate help as a simple replacement for the high power arc sources used in earlier photodetachment work. The recent development of dye lasers, tunable over spectral ranges of several hundred angstroms, contains more promise for spectroscopic scanning. The limitations for present purposes lie in the fact that the few hundred angstrom range available with a Rhodamine G dye laser, for example, corresponds to an energy range of the order of only a tenth of an electron volt in the visible spectrum. This is too small to encompass enough vibrational structure to permit determination of such constants as vibrational spacing and anharmonicity. The spectral range can be extended by the use of a sequence of dyes, but this compounds the difficulties in an already difficult measurement, and wide spectral range studies in molecular negative ion photodetachment by this means have not been forthcoming. E. C. Beaty and G. Sinnott⁷ have observed a threshold for photodetachment from O_3^- equilibrated in oxygen at room temperature, at about 2.07 eV, within the range of the Rhodamine G dye laser. Attempts to extend the range of this measurement with other dyes have yet to succeed.

The development of more versatile continuously tunable lasers can be presumed for the future, and ultimately, scanning lasers should be a powerful tool for molecular photodetachment work.

The important breakthrough, fully realized within the past year or two, has come about through a modification of the photodetachment technique to include high resolution energy analysis of electrons photodetached by a

fixed frequency laser. For best results the photon energy $h\nu$ must be sufficient to remove an electron from the negative ion and to excite the residual neutral molecule to any of several vibrational levels. In the simplest case the negative ion will be a diatomic ion in its lowest vibrational level ($v'' = 0$). The range of vibrational levels accessible in the residual molecule will depend on the Franck-Condon overlap factors as well as on the photon energy. In any case the conventional photoelectric equation,

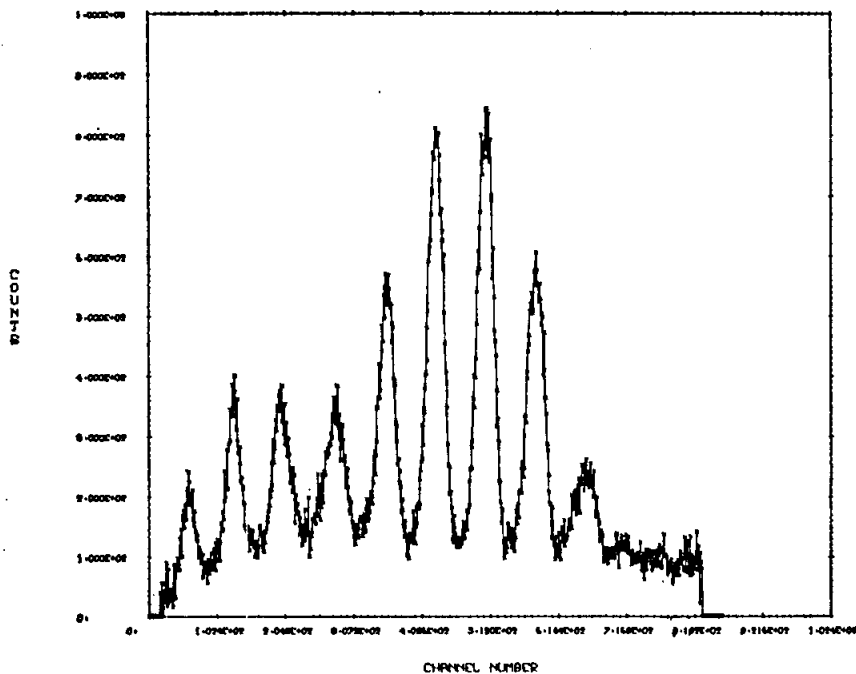
$$\text{K.E.} = h\nu - \Delta E,$$

tells us that with a fixed frequency laser each discrete transition, of energy ΔE , which occurs with high probability will give rise to a corresponding discrete component in the kinetic energy (K.E.) spectrum of photodetached electrons. This method has been developed by J. L. Hall *et al.*,⁸ and applied with great success to the study of NO^- and O_2^- in a crossed laser beam-ion beam configuration.

Figure 1 shows an electron energy spectrum obtained using an argon ion laser crossed with a beam of O_2^- . The O_2^- ions are initially predominately in the $v'' = 0$ vibrational level of the $^2\Pi_g$ ground state of the negative ion (see Fig. 2). The peaks in the electron energy spectrum are readily identifiable by comparison of the spacing with the known vibrational spacings of the $^3\Sigma_g^-$ ground state of O_2 . Identification was confirmed by studies of the effects of isotope substitution on the observed spacings. The first obvious peak on the right of the spectrum in Fig. 1 corresponds to the $v'' = 0 \rightarrow v' = 0$ transition, where v' represents the vibrational levels of the $^3\Sigma_g^-$ state of O_2 . Sequentially to the left of this the peaks correspond to transitions to $v' = 1, 2, 3, 4$. Beyond this, transitions to the $v' = 0, 1, 2, 3$ levels of the $^1\Delta_g$ state are evident. A small component of $v'' = 1$ population in the O_2^- beam is responsible for the very small structure at the right of the scan and for the broadening of the $v' = 0$ peak.

While the vibrational structure observed is that of O_2 , not of O_2^- , nevertheless some important information about O_2^- is available from data such as that of Fig. 1. The energy scale can be calibrated quite accurately by photodetachment of S^- and O^- for which the binding energies are well known.⁹ Calibration of the energy scale permits a very precise determination of the energy interval for each of the vibrational transitions represented in Fig. 1. The system of energy levels of the negative ions are reliably fixed with respect to those of the neutral molecule. Celotta *et al.*⁸ find the $v'' = 0 \rightarrow v' = 0$ interval, which they define as the electron affinity EA, is equal to 0.43 eV.

Further information comes from consideration of the shape of the envelope of each of the two vibrational sequences represented in Fig. 1. These envelopes are determined by the Franck-Condon factors which are highly dependent



02- DATA OF 12/3/69 EXPONENTIAL BACKGROUND SUBTRACTED OUT.

FIG. 1. Current is plotted against energy for electrons outgoing after photodetachment from O_2^- . The scale is linear and represents a 2.5 eV range in electron energy. The first clearly significant peak on the right is the (O-O) transition corresponding to the electron affinity.

on internuclear separation r_e of the negative ion. They find $r_e(O_2^-) = 1.34 \pm 0.01 \text{ \AA}$. The Franck-Condon fitting process is also sensitive to the shape of the Morse potential. Therefore the fitting procedure yields an estimate of ω_e and $\omega_e x_e$ for the negative ion, and this has proved to be in fair agreement with direct results of methods of measurement discussed below.

In principle, direct information about the vibrational spacing of the negative ion could be obtained if larger components of vibrationally excited ions were present in the beam. This would complicate the spectrum and would often degrade the accuracy with which peak energies could be measured. This method is most accurate in the determination of r_e and EA for a diatomic negative ion. A number of diatomic ions are accessible to the technique. With improvements in resolution valuable information about

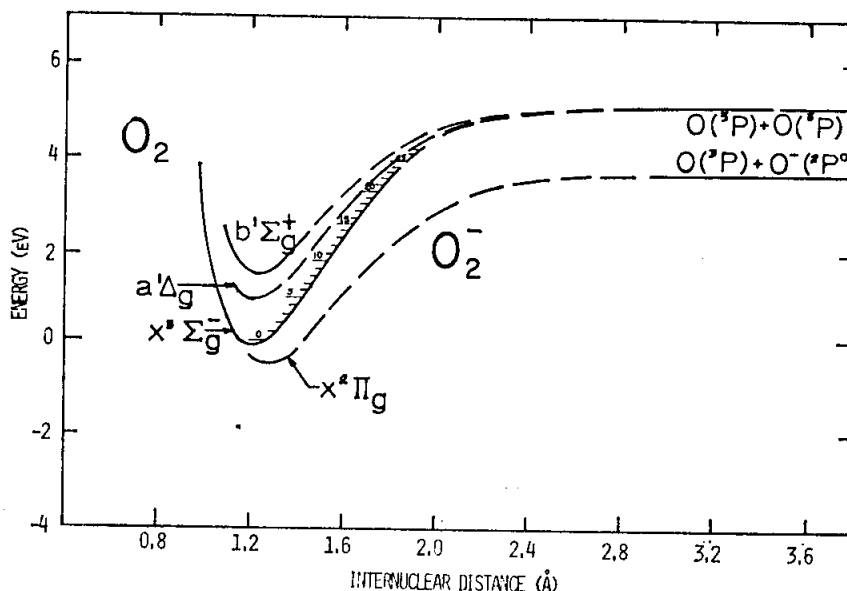


FIG. 2. A few of the relevant potential curves for O₂ and O₂⁻ are represented.

more complex ions as well as more direct information about vibrational intervals in negative ions may be forthcoming.

The absence of direct information from photodetachment about vibrational spacing and anharmonicity for the diatomic negative ions, necessary for the construction of Morse potential curves, would leave affairs in a less than satisfying state, were it not for the parallel development, also within the last several years, of high resolution low energy electron scattering techniques which yield this information. Results of several different types of such electron-neutral molecule scattering studies¹⁰⁻¹³ show structure which can be related to the vibrational structure of the negative ion. As one example, Boness and Schulz studied the component of electron current scattered elastically from a beam of neutral oxygen molecules at an angle of about 50° to the incident beam over a range of electron energies from near zero up to about 1.5 eV. The scattered current plotted against electron energy exhibits five peaks spaced at intervals of 0.12, 0.12, 0.11, and 0.11 eV. The peaks are interpreted as resonant responses in the scattering probability to the coincidence of the electron energy with the energy interval between the zero vibrational level of oxygen and one of the several vibrational levels of O₂⁻. A temporary negative ion may be said to be formed as an intermediate stage of the scattering process.

These observations determine a sequence of vibrational intervals for O₂⁻

but the vibrational quantum numbers are not directly determined. Numbers can be assigned, however, by referring to the electron affinity determined from the laser photodetachment studies. Once this assignment is made a fairly complete picture of the negative ion energetics can be constructed.

The two types of experiment have proven to be quite complementary. The errors in the photodetachment results for ω_e and $\omega_e x_e$ are difficult to evaluate, but these are just the quantities measured with precision by the electron scattering experiments. On the other hand the electron scattering work cannot determine the electron affinity or the negative ion internuclear separation, and these quantities are accurately determined by the photodetachment work.

At the present time both types of measurements have been carried out for NO^- and O_2^- . The data are still capable of improvement. They will undoubtedly be refined, but the fact that such complete experimental information is becoming available with regard to a few members of an entire class of molecules previously accessible only to theoretical estimates must be counted a quite significant development.

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