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COMMUNICATIONS

Direct measurement of the binding energy of the NO dimer

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The binding energy of the NO dimer has been measured directly using velocity-mapped ion imaging. NO dimer is photodissociated to produce NO(X) and NO(A), and the NO(A) is then nonresonantly ionized to NO^+. The threshold for production of NO^+ ions is measured at 44 893 $\pm 2\ cm^{-1}$, which corresponds to a binding energy of $696\pm 4\ cm^{-1}$. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1459702]

NO is an important molecule in a wide range of atmospheric and biological processes, and as a result the reactivity of the NO dimer, $(NO)_2$, has been of interest since the 1950s.[1–3] NO is an open shell molecule, so the formation of the dimer involves the formation of a bond from the unpaired electron of each NO monomer. This bond is stronger than is usual for a typical van der Waals molecule.

The dissociation and reactivity of $(NO)_2$ in the gas phase has been investigated using a variety of experimental spectroscopic techniques.[1–9] Several of these studies have included indirect measurements of the binding energy of $(NO)_2$, $D_0[(NO)_2]$, through analysis of its ultraviolet[5] and photoelectron[6] spectra, analysis of its ν_1 and ν_5 vibrational bands,[7,8] or direct study of vibrational predissociation of $(NO)_2$ in infrared photodissociation experiments.[9,10] These previous experiments indicate that the binding energy of $(NO)_2$ is in the range of $560-800\ cm^{-1}$, which is larger than a typical van der Waals interaction and smaller than a typical chemical bond. Several of the previously determined values for the binding energy of $(NO)_2$ are given in Table I. There is considerable disagreement between these previously measured values. The two most recent measurements differ from each other by more than $100\ cm^{-1}$.

In this work, we have applied velocity-mapped ion imaging following nonresonant ionization to directly observe the threshold for dissociation of $(NO)_2$. Ion imaging has been applied to a wide range of photodissociation processes,[11] and is typically coupled with resonance-enhanced multi-photon ionization (REMPI) to detect state-selected products.

In this experiment, $(NO)_2$ is produced in a doubly skimmed molecular beam by expanding 3%–5% NO in Ar, with a backing pressure of 1.0–1.5 atm. It is then photolyzed with a ~222 nm laser pulse, with a pulse energy of <1 mJ, to produce NO(A) from the photodissociation reaction:

$$(NO)_2 \rightarrow NO(A) + NO(X).$$

The frequency of the laser beam is monitored with a New Focus Fizeau 7711 wavemeter, to $\pm 0.5\ cm^{-1}$, and the calibration was confirmed by comparison of the wavemeter correction and the assignment of the REMPI spectrum of NO monomer. The NO(A) is ionized nonresonantly by the same laser pulse. The NO^+ ions are accelerated toward the detector, which is time-gated so that only ions with the same mass as NO are detected, and velocity-mapped onto a two-dimensional position-sensitive detector. The resulting ion images just below, at, and above the threshold for production of NO(A) from $(NO)_2$ are shown in Fig. 1. The outer ring in all three images is due to NO(A) from the dissociation of the $NO \cdot Ar$ clusters, which photodissociates at a much lower energy $(\sim 100\ cm^{-1})$[12] and has much greater translational energy at this laser frequency. In the first image, no center spot is observed. In the second image, a faint center spot can be seen, and it grows brighter and slightly larger in the third image. This central feature is also observed at the same threshold wavelength when the carrier gas is changed to He, and the threshold wavelength is also independent of stagnation pressure. We therefore assign this central feature to NO^+

TABLE I. Measurements of the $(NO)_2$ binding energy.

Reference	Year published	$D_0[(NO)_2]$ (cm^{-1})
This work	2002	696 ± 4
Dkhissi *et al.* (8)	1997	764 ± 18
Howard *et al.* (7)	1993	639 ± 35
Fischer *et al.* (6)	1992	787
Hetzler *et al.* (10)	1991	710 ± 40
Casassa *et al.* (9)	1988	800 ± 150
Billingsley *et al.* (5)	1971	560 ± 33

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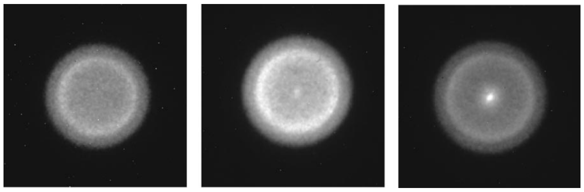

FIG. 1. Images collected following ionization of NO at ~222 nm, showing the threshold of photodissociation of $(NO)_2$ to $NO(X)+NO(A)$. The images are scaled so that the brightest pixels are full white. The first image is below the photodissociation threshold, at 222.768 nm, so no central spot is observed. The second image is just at threshold, at 222.745 nm, and a faint central spot, due to NO^+ from the photodissociation of $(NO)_2$ can be observed. The third image, at 222.718 nm, is $\sim 10\ \mathrm{cm}^{-1}$ over the threshold and the central spot is becoming larger and more intense. The outer ring in all three images is due to $NO(A)$ produced by the photodissociation of $NO\cdot Ar$, which is much more weakly bound than $(NO)_2$ and so has more recoil energy at the same laser frequency.

from the photodissociation of $(NO)_2$, which is being produced from nonresonant ionization of $NO(A)$ just above the photodissociation threshold and therefore has very little translational energy.

Since a photon of ~222 nm light has more than enough energy to ionize $NO(A)$, the amount of recoil energy, E_{rec}, observed in the $(NO)_2$ image is the sum of the initial internal energy of $(NO)_2$, E_{initial}, and the energy of the photon, $h\nu$, minus the sum of $D_0[(NO)_2]$, the energy difference between the $NO(X)$ state and the $NO(A)$ state, $T_0[NO(A)\leftarrow NO(X)]$ and the internal energy of the NO products, E_{NO}

$$E_{\mathrm{rec}}=E_{\mathrm{initial}}+h\nu-\{D_0[(NO)_2]+T_0[NO(A)\leftarrow NO(X)]+E_{\mathrm{NO}}\}. \tag{1}$$

These energy levels are shown schematically in Fig. 2.

By examining the ion images to determine the wavelength for which E_{rec} approaches zero, where the central spot in the images disappears, we find that the threshold energy, or the laser frequency associated with $E_{\mathrm{rec}}=0\ \mathrm{cm}^{-1}$, is $44893\pm 2\ \mathrm{cm}^{-1}$ or 222.75 ± 0.01 nm. $T_0[NO(A)\leftarrow NO(X)]$ is very well established at $44\,200.2\ \mathrm{cm}^{-1}$,[13] so $\{D_0((NO)_2)-E_{\mathrm{initial}}\}$ is $693\pm 2\ \mathrm{cm}^{-1}$. E_{initial} is the sum of vibrational and rotational energy for $(NO)_2$. The smallest frequency normal mode of $(NO)_2$ is ν_4, which is $117\ \mathrm{cm}^{-1}$ for the *cis* isomer[14] and $79\ \mathrm{cm}^{-1}$ for the *trans* isomer.[15] If we were observing dissociation from vibrational hot bands, we would expect to see separate rings for each vibrationally excited state, as the detection system can easily resolve rings corresponding to an energy spacing of $>10\ \mathrm{cm}^{-1}$. Since we do not observe such rings, the only remaining source of internal energy for $(NO)_2$ is rotational excitation. It is not possible for us to directly measure the extent of rotational excitation, but we can estimate it. REMPI measurements of the spectrum of NO monomer in our molecular beams give us a rotational energy of 3 ± 1 K. Using the available rotational constants for $(NO)_2$,[7] and approximating $(NO)_2$ as a prolate top, it is possible to calculate a Boltzmann distribution for $(NO)_2$ rotational states at 3 K. If we assume that we do not detect signal due to rotationally excited states that are less than 5% of the total population, we find an upper limit of rotational excitation of $3\pm 2\ \mathrm{cm}^{-1}$, which would indicate that $D_0[(NO)_2]$ is $696\pm 4\ \mathrm{cm}^{-1}$. However, it is likely that, if $(NO)_2$ were rotating with $3\ \mathrm{cm}^{-1}$ of rotational energy, the rotation would result in centrifugal acceleration of the dissociation products which would in turn result in translational energy. Since we can directly observe $NO(A)$ produced just above threshold with $<2\ \mathrm{cm}^{-1}$ of translational energy, it is likely that at threshold we are observing $NO(A)$ produced from $(NO)_2$ with very little initial rotational energy. If that is the case, then $D_0((NO)_2)$ equals our directly measured threshold energy and is $693\pm 2\ \mathrm{cm}^{-1}$.

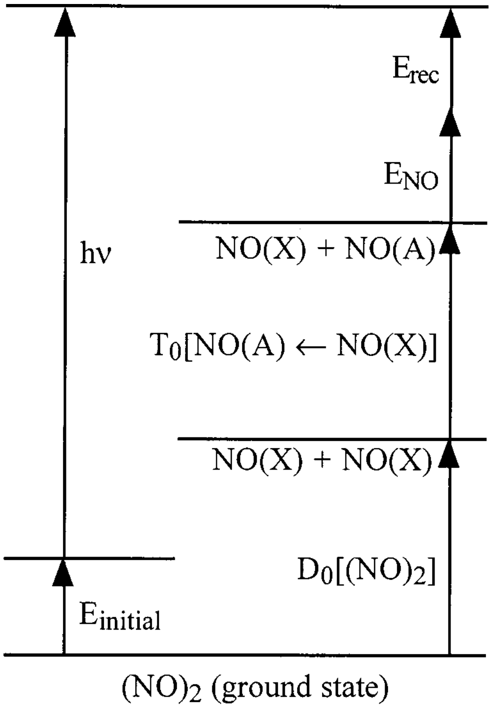

FIG. 2. Schematic of energies involved in the photodissociation of $(NO)_2$ to $NO(X)+NO(A)$, as described in Eq. (1).

We also assume that the NO^+ we observe at the threshold wavelength is due to NO products in their rotational and vibrational ground state, so that $E_{\mathrm{NO}}=0$. It is possible that dynamic constraints make it impossible for the dissociation of $(NO)_2$ to produce NO in its ground rotational state. Since this would mean $E_{\mathrm{NO}}>0$, it would mean that our value of $D_0((NO)_2)$ is larger than the true value. However, we observe NO^+ with $<2\ \mathrm{cm}^{-1}$ of translational energy, which suggests that there is at most a very small barrier to dissociation, and which in turn suggests that just at the dissociation threshold there is no impulse that would force the NO products to be rotationally excited.

Hetzler *et al.* observed product rotation distributions of the NO fragments following dissociation of overtone-excited $(NO)_2$.[10] They accounted for the observed distributions by postulating a $900\ \mathrm{cm}^{-1}$ barrier to the association of NO fragments to form the dimer. Our results strongly suggest that there is at most a very small ($<2\ \mathrm{cm}^{-1}$) barrier to the reverse reaction.

Similarly, we assume that the first NO^+ we observe is due to the dissociation of the dimer to produce $NO(A)+NO(X,\Pi_{1/2})$, not $NO(A)+NO(X,\Pi_{3/2})$. If for some reason, the $NO(X)$ is produced exclusively in the spin-orbit excited state, then $E_{\mathrm{NO}}=119.7\ \mathrm{cm}^{-1}$,[13] and our observed threshold would correspond to a dissociation energy of $573 \pm 5\ \mathrm{cm}^{-1}$. This value is substantially lower than previous measurements. It seems unlikely that this dissociation would produce no NO in the spin-orbit ground state, since statistical dissociation mechanisms would favor formation of the spin-orbit ground state rather than the spin-orbit excited state.

This threshold measurement was also confirmed by our observation of NO(B) from $(\mathrm{NO})_2$ photolysis. The B-state of NO is less than $1500\ \mathrm{cm}^{-1}$ above the A-state.[13] By setting the laser frequency to the predicted energy, we were able to observe a new central peak due to the ionization of NO(B). Unfortunately, the threshold of the $(\mathrm{NO})_2 \rightarrow \mathrm{NO}(B) + \mathrm{NO}(X)$ channel overlaps with a $1+1$ REMPI transition in NO monomer, producing an NO^+ signal which overwhelms the NO^+ signal rising from the photodissociation of the dimer. As a result, we were not able to directly observe this channel's threshold. However, the observed recoil energy distribution for the new channel is consistent with our value of $D_0[(\mathrm{NO})_2]$.

In summary, we have directly observed NO produced by the photodissociation of NO dimer, and have determined a measurement of the binding energy of the NO dimer at $696 \pm 4\ \mathrm{cm}^{-1}$.

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