Driven Morse Oscillator:  
Model for Multi-photon Dissociation of Nitrogen Oxide

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Within a one-dimensional semi-classical model with a Morse potential the possibility 
of infrared multi-photon dissociation of vibrationally excited nitrogen oxide was studied. 
The dissociation thresholds of typical driving forces and couplings were found to be 
similar, which indicates that the results were robust to variations of the potential and of 
the definition of dissociation rate.

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1. Introduction

Experimental microwave multi-photon dissociation of nitrogen oxide (NO) is not yet 
possible, whereas the corresponding optical photodissociation is readily observed via elec-
tronic transitions. However, it is important to know the possibility and how one can make 
it, firstly because NO is abundant in nature and in living bodies, and secondly because 
the intensity of lasers has reached the order of magnitude needed to do the experiment. 
Although hydrogen fluoride (HF) has a smaller dissociation energy, from an experimental 
view, because of the stability, simplicity and well documented properties of NO, easier 
preparation of intense molecular beams of NO than of HF, and more efficient probing, 
NO has been chosen for investigation instead of HF. Although experiments were formerly 
conducted as NO mostly in the ground state prepared by supersonic expansion, it has be-
come possible to transfer population efficiently to other states: Yang et al. (1990) report 
experiments in which NO molecules were populated into an initial vibrational state as 
great as \( n = 25 \) by stimulated-emission pumping (SEP) whereas Schiemann et al. (1993) 
showed recently how to populate to a state \( n = 6 \) by a stimulated Raman process in-
volving adiabatic passage (STIRAP) method using pulsed lasers. In our study we chose 
parameters for NO whenever molecular properties were needed for our calculations, so 
that future experiments can be easily compared with the results presented here. The 
behaviour of NO is expected to be typical of that of other diatomic molecules.

Theoretically much previous work concentrated on the corresponding atomic systems. 
Similar to the present work Blümel and Smilansky (1987) did a calculation on the hydro-
gen atom and Broeckhove (1992) made a calculation on HF. But no previous calculation 
of the dissociation thresholds of every initial eigenstates has been performed. In this pa-
per the Morse potential-energy function for the inter-atomic interaction was used; only 
the vibrational levels were considered presently because Morse (1929) and Pekeris (1946)

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Table 1. Typical parameters for NO.

| parameter                        | symbol | value               |
|----------------------------------|--------|---------------------|
| range parameter of the potential | α      | 2.7675 $\times 10^8$ cm$^{-1}$ |
| reduced mass                     | m      | 7.4643 u            |
| dissociation energy              | D      | 6.4988 eV           |
| Morse frequency                  | $\omega_0$ | 1904.2 cm$^{-1}$   |

have pointed out that the rotational influence on vibration can be taken into account by suitably adjusting the Morse parameters.

The Morse potential was used by Lennard-Jones and Strachan (1935), Strachan (1935) to investigate the interaction of atoms and molecules with solid surfaces in the early days. Isnor and Richardson (1971), Walker and Preston (1977) studied the driven Morse oscillator as a model for infrared multi-photon excitation and for dissociation of molecules, stimulated by the possibility of laser isotope separation and bond-selective chemistry. The Morse potential lacks the complication of infinitely many bound eigenstates and the singularity of the Coulomb potential at the origin of the hydrogen atom.

The methods to calculate multi-photon dissociation are generally divided into non-linear classical-mechanical methods, like that of Goggin and Milonni (1988) and semi-quantum methods like that of Heather and Metiu (1987), Heather and Metiu (1988), Tanner and Maricq (1988). The latter approach is used in this study.

2. Model

We consider an isolated non-rotating NO molecule interacting with a plane-polarised harmonic laser field. The dimensionless Hamiltonian of a free Morse oscillator for a diatomic molecule is

$$H_0 = \frac{p_z^2}{2} + \frac{(1 - e^{-z})^2}{2},$$

(1)

in which $z = \alpha (r - r_e)$ denotes displacement of inter-atomic distance from equilibrium, $p = p_z/\sqrt{2mD}$, and $p_z$ is the momentum conjugate to $z$. The parameters of NO are given by Huber and Herzberg (1979) and summarised in the TABLE. The Hamiltonian for the Morse oscillator in the presence of a typical harmonic laser field reads

$$H = H_0 - \frac{A \Omega}{2} \mu(z) \Phi(\Omega t),$$

(2)

in which $\mu$ is the dipole moment operator. In the formula above two dimensionless variables are introduced, namely $\Omega = \omega_L/\omega_0$ with $\omega_L$ the laser frequency, and the dimensionless field strength $A = qE_L/\alpha \Omega D$ with $E_L$ the field strength of the laser and $q$ is the effective dipole charge of the molecule. In the numerical calculations below various types of couplings are considered.

The discrete eigenfunctions of the free Morse oscillator were given by Morse (1929) and denoted by $|n>$ with the corresponding dimensionless eigenvalues equal to

$$E_n = \frac{\bigg( n + \frac{1}{2} \bigg)^2}{\lambda^2} - \frac{\bigg( n + \frac{1}{2} \bigg)^4}{2\lambda^2},$$

(3)

in which $\lambda = \sqrt{2mD/\alpha \hbar} = 55.04$. The term multi-photon is generally applied to this
system, as each photon has energy about 0.24eV near the Morse frequency ($\omega_0$), whereas the energy difference between the ground state and the first excited state of the free Morse oscillator is about 0.23eV; about 28 photons must be absorbed for the transition from the ground state to the continuum.

Our main concern is the transition between each excited state of the free Morse oscillator and dissociation. With various initial states $|n>$, driving frequencies and driving amplitudes the dissociation periods required might change dramatically. The problems of this calculation are whether our model can really represent the molecular system for which we intend it for and what is our definition of dissociation. How robust are the results? To address these questions we present two typical definitions of dissociation and driving forces.

3. Numerical results

The following numerical results were obtained using a method described and verified previously by Ting et al. (1992), which is a fast Fourier-transformed grid method also considered by Feit et al. (1982), Leforestier et al. (1991).

3.1. Dipolar coupling

Following Walker and Preston (1977), Goggin and Milonni (1988) on a driven Morse oscillator, as a consistency check in the first instance, a cosinusoidal waveform was used. Hence the Hamiltonian in Eq. (2) reads

$$H = H_0 - \frac{A\Omega}{2}z\cos(\Omega t).$$

(4)

According to Goggin and Milonni (1988), Chelkowski and Bandrauk (1990) for quantum chaos the definition of dissociation rate is

$$P_{diss}(t) = 1 - \sum_n |<n|\psi(t)>|^2.$$  

(5)

We define $P_{diss}(t) = 0.05$ for the molecule to satisfy the dissociation condition. If the molecule cannot reach such a dissociation rate within 300 cycles we consider it to be not dissociable under such conditions of field intensity and frequency. This definition is almost equivalent to comparing the dissociation rate after 300 cycles. According to Leforestier et al. (1991) the latter should be easier to calculate. However, these two definitions are distinct. Furthermore, the definition of $P_{diss}$ is only approximate because, when the field is applied, the projection onto the bound states fails to represent the true bound-state population unless one assumes that the electro-magnetic field can be terminated instantaneously. The values 300 and 0.05 are set according to previous experience, although there are some guiding principles: 300 cycles corresponds to a pulse of duration about 5 picosecond, which is the time scale for bound dissociation to occur. These choices are analogous to those used in the calculation of atomic ionisation by Blümel and Smilansky (1987).

The dissociation histories from Eq. (5) were calculated at $\Omega = 0.9$. Fig.1 shows dissociation histories of four types at critical amplitudes, i.e., the largest amplitude at which the molecule just fails to be dissociated within 300 vibrations. There are several such critical amplitudes for some low-lying initial states (vide infra). This classification is not rigorous, but represents at least some typical dissociation histories; it results from investigation of more than 500 curves obtained for the calculation for Fig.3. Ting et al. (1992) shows other curves. A brief description of each type follows. For the first type the curve
Figure 1. Dissociation histories of four types observed at critical amplitudes $A = A_c$ and laser frequency $\Omega = 0.9$: (a) the curves rise smoothly; (b) the curves rise sharply; (c) curves that are distinct from those of neighbouring states; (d) straight lines.

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Figure 2. Dissociation histories of initial states from 24 to 29 at $A=0.01$ and $\Omega = 0.9$; the state with $n_0 = 28$ dissociate more readily than its neighbouring states.

Figure 3. Critical amplitude ($A_c$) for various initial states at $\Omega = 0.9$; the Hamiltonian is Eq. (4), and the dissociation rate is Eq. (5); for low-lying states which have two values of $A_c$ only the lower one is connected.

Inter-atomic distance shows that, immediately after the field is switched on, states with $n_0 > 25$ move in a direction distinct from that for $n_0 < 25$ away from the inter-atomic equilibrium position.

In Fig.3 the critical fields required for the molecule to become dissociable is plotted. For multi-critical states the lowest ones are connected and the others marked. Therefore the plot provides only a sufficient criterion for dissociation, not a necessary condition. The reason is that as we use numerical methods we can know only the points that we computed. The amplitude resolution of our calculation is $\Delta A = 0.0005$. If there were a narrow transition less than 0.0005 one might not be able to find it, because such a point would imply experimentally a laser of precise power. We find at most two critical amplitudes in the present case while in another study using two-color laser fields we find up to three. The multi-critical amplitude is also a result of our selection of the critical dissociation period to be 300. However, this point implies that decreasing field strength does not necessarily increasing the dissociation period. Lu et al. (1991) noted that the finite size of $\bar{\hbar}$ probably places a characteristic scale in parameter space less than which the dissociation boundary ceases to show fractal structure. Another feature of the figure is that the largest value of $A_c$ is several orders of magnitude larger than the smallest one.
Figure 4. Critical amplitude ($A_c$) for various initial states at (a) $\Omega = 0.89$ (solid thick line) and (b) $\Omega = 0.91$ (thin dashed line); the Hamiltonian is Eq. (4) and the dissociation rate is Eq. (5).

Figure 5. Critical amplitude ($A_c$) vs. frequency of initial states (a) $n_0 = 1$, (b) $n_0 = 17$ and (c) $n_0 = 24$.

A calculation shows that for $n_0 \geq 6$ the photon energy becomes larger than the energy difference between adjacent states.

To discover whether $\Omega = 0.9$ is the most efficient frequency for all initial states we tested $\Omega = 0.89$ and $\Omega = 0.91$. The critical amplitudes are plotted in Fig.4. As we had insufficient computer time to test all states and all frequencies, we selected $n_0 = 1, 17$ and 24 to find whether values of $A_c$ alter for frequencies from 0.8 to 1.1 at interval 0.01. The plots appear in Fig.5.

3.2. Exponential coupling

The perturbation in Eq. (4), although simple and easily done by the Floquet method, has several problems in relation to reality. Firstly, the molecular dipole and laser coupling in equation Eq. (4) assumes a infinite range of constant coupling, which is satisfactory for an atomic system but not for a real molecule. Secondly, as Sakurai (1967) has noticed, the field should be zero at $t = 0$ and gradually increases from zero to a finite value; this problem is called adiabatic switching. Therefore, another exponential form of coupling

$$H = H_0 - \frac{A\Omega}{2}(z + a)e^{-(z+a)/b} \sin(\Omega t) \sin^2\left(\frac{2\pi t}{T}\right),$$

(6)
was used to test whether there is any effect of the approximation. The problem of the definition of dissociation rate was pointed out above (below Eq.(5)); here we alter it to comply with Heather and Metiu (1987)

\[ P_{\text{diss}}(t) = 1 - |\langle \psi(t)|\psi(t) \rangle|. \] (7)

This definition is appropriate if coherent excitation becomes important. The variables \( a \) and \( b \) were chosen to have the values 2 and 1 respectively in the calculation. Heather and Metiu (1987), Heather and Metiu (1988), Tanner and Maricq (1988), Tanner and Maricq (1989) have also used coupling functions of similar form. We take \( T_d \), the pulse duration, to be 300 optical cycles. This choice has the advantage that, when \( A = A_c \), \( T_d \) is almost 300 cycles and the field strength is almost zero at that time. Hence there is little effect of the definition of dissociation rate. The resulting critical front appears in Fig.6 as a solid thick line. There is no essential distinction from Fig.3 and Fig.4 except a scaling parameter that can be adjusted by choosing \( a \) and \( b \). For lower initial states there is more variation than for higher initial states. To assess whether \( T \) is large enough, a longer period \( T = 600 \) is tested. The result is plotted in Fig.6 with a thin dashed line; the two lines show similar behaviour.

4. Summary

In conclusion, thresholds of vibrational dissociation of NO are considered in this paper. The main result of this paper is depicted in Fig.6. Two perturbations and definitions of dissociation rate lead to similar curves with the transition from high \( A_c \) to low \( A_c \) shifted slightly to higher initial states. Laser fields and couplings of other kinds were tested for which similar curves were obtained. Therefore, as our main concern is the critical amplitude which is an indirect result, we conclude that our results are robust to variation of the potential function. Variations of other types such as the laser duration and definition of dissociation threshold are less significant. A rough estimate of the decrease of \( A_c \) is given. The assumption behind this model is that no other electronically nonadiabatic effects will occur first. One must take care in comparing the results presented in this work with those from experiment. For instance, because of the finite cross section of the beam, not all molecules experience the same field strength. The ignorance of rotational influence should also be remembered. The additional selection rule in the rotating case may make the progression to dissociation harder.
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REFERENCES

Blümel R and Smilansky U 1987 Z. Phys. D 6, 83.
Broeckhove J, Feyen B and Van Leuven P 1992 J. Mol. Struct. 261, 265.
Chelkowski S and Bandrauk A 1990 Phys. Rev. A 41, 6480.
Feit M D, Fleck J A Jr. and Steiger A 1982 J. Comp. Phys. 47, 412.
Goggin M E and Milonni P W 1988 Phys. Rev. A 37, 796.
Heather R and Metiu H 1987 J. Chem. Phys. 86, 5009.
Heather R and Metiu H 1988 J. Chem. Phys. 88, 5496.
Huber K P and Herzberg G 1979 Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules, Van Nostrand Reinhold Co.
Isnor N R and Richardson M C 1971 Appl. Phys. Lett. 18, 224.
Leforestier C 1991 et al., J. Comp. Phys. 94, 59.
Lennard-Jones J E and Strachan C 1935 Proc. Roy. Soc., London A150, 442.
Lu Z-M, Heagy J F, Vallières M and Yuan J-M 1991 Phys. Rev. A 43, 1118.
Morse P M 1929 Phys. Rev. 34, 57.
Pekeris C L 1946 Phys. Rev. 70, 222.
Pfeifer P 1993 Phys. Rev. Lett. 70, 3365.
Sakurai J J 1967, Advanced Quantum Mechanics, Addison Wesley, New York, p200.
Schiemann S, Kuhn A, Steuerwald S and Bergmann K 1993, Phys. Rev. Lett., 71, 3637.
Shanker R 1980 Principles of Quantum Mechanics, Plenum Press, New York, p491.
Strachan C 1935 Proc. Roy. Soc., London A150, 456.
Tanner J J and Marićq M M 1989 Phys. Rev. A 40, 4054.
Tanner J J and Marićq M M 1988 Chem. Phys. Lett. 149, 503.
Ting J J-L, Yuan J M, and Jiang T F 1992 Comput. Phys. Comm. 70, 417.
Walker R.B. and Preston R.K. 1977 J. Chem. Phys. 67, 2017.
Yang X, Kim E K and Wodtke A M 1990 J. Chem. Phys. 93, 4483.