

ANHARMONICITY EFFECT ON VIBRATIONAL RELAXATION
IN CARBON MONOXIDE

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A previous model for calculating the cross sections of the vibrational excitation of carbon monoxide by collision with carbon monoxide has been improved to include anharmonicity effects in the vibrational wavefunctions by describing them in terms of Morse oscillators.

It is shown that this leads to further improvement in the agreement between the theoretical and experimental values for the vibrational relaxation times.

The sensitivity of the total cross sections to anharmonicity is investigated at several collision energies and further lines of approach are suggested.

1. INTRODUCTION

The mechanism of the interconversion of vibrational and translational energy in gases is of great importance both in unimolecular rate theory and in connection with relaxation processes in gaseous systems; the extensive literature on the subject has been summarized by Cottrell and McCoubrey [1] and the theoretical search for model calculations has recently attracted the attention of many researchers working in this field [2].

In the numerical method described by Marriott [3, 4] the molecular wavefunction was assumed to be separable into electronic, rotational and vibrational components, the coupling between vibrational and rotational states neglected, and the molecular target assimilated to a "breathing sphere" interacting via a 6-12 type potential with the incoming projectile.

Recently theoretical inelastic cross sections for vibrational excitation of CO molecules have been recalculated within the above model, with the intention of quantitatively gauging their dependence upon the parameters connected with the numerical computation [5]: the empirical nature of the Lennard-Jones potential requires, in fact, a choice of ϵ 's and σ 's spanning the temperature range relevant to relaxation time measurements [6]. These calculations seemed to show that the

order of magnitude of the total cross section for the $\nu \rightarrow \nu'$ ($0 \rightarrow 1$) vibrational excitation is scarcely affected by parameter variation within the suggested intervals, thus leaving unchanged the agreement with experimentally obtained relaxation times.

In the present note, the molecular oscillator has been, more realistically, described by a Morse-type wavefunction [7] as opposed to the simple harmonic oscillator previously used [3-5] and calculations of inelastic cross sections for the CO ($0 \rightarrow 1$) vibrational excitation by CO have been carried out for a large range of collision energies.

2. THE ANHARMONIC OSCILLATOR
FOR CARBON MONOXIDE

If the Morse potential for a diatomic molecule is written as

$$V(R) = D \left\{ e^{-2a(R-R_0)} - 2e^{-a(R-R_0)} \right\} \quad (1)$$

with D , a and R_0 being spectroscopically determined parameters, while R is the interatomic distance, the corresponding eigenvalue equation for a spherically symmetric molecular state with rotation quantum number $j = 0$ has radial solutions in a finite polynomial form under the condition:

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$$\frac{8\pi\mu D}{a^2 h^2 d} - \frac{b}{2} - \frac{1}{2} = n,$$

where n is an integer greater than zero [7]. The positive (non-integer) values of b are the ones for which the radial eigenfunction is finite over the range $0 \leq Z \leq \infty$, with $Z = 2d \times \exp[-a(R - R_0)]$, d being defined as in ref. [7].

The complete solutions contain generalized Laguerre polynomials [8], through which the normalization constant has to be obtained.

Both Ψ_{Morse}^n and N_{nm} are as in eqs. (2), and rather different from the expressions given in ref. [7] which appear to be in error*

$$\Psi_{\text{Morse}}^n =$$

$$\left(\frac{1}{N_{nm}}\right)^{\frac{1}{2}} e^{-d} \exp[-a(R-R_0)] \left[2d e^{-a(R-R_0)} \right] \times b_{n/2} \times L_{n+b_n}^{b_n} \left[2d e^{-a(R-R_0)} \right] \quad (2a)$$

$$N_{nm} = \frac{[\Gamma(b_{n+n+1})]^3}{(b_n)n!} \quad (2b)$$

$$L_{n+b}^b(z) = \frac{d^b}{dz^b} \left[e^z \frac{d^{n+b}}{dz^{n+b}} (z^{n+b} e^{-z}) \right]. \quad (2c)$$

In the present collisional model, the short-range interaction potential is considered to be mainly responsible for the inelastic scattering, so that each partial-wave cross section is obtained from potential matrix elements of the type

$$V_{nm} = \langle \Psi_n(R) | V(R) | \Psi_m(R) \rangle \quad (3)$$

with $\Psi_n(R)$, $\Psi_m(R)$ being two Morse oscillators in the n th and m th levels respectively.

$V(R)$ is found by assuming the total potential to be of the form

$$V(r, R) = V_1(r) V_2(R) \quad (4)$$

with r being the distance between the projectile and the target centre of mass.

We now assume

$$V(r, R) \approx V(r, R_0) + \left. \frac{\partial V(r, R)}{\partial R} \right|_{R=R_0} \times (R - R_0) \quad (5a)$$

$$= V(r, R_0) \left\{ 1 + \left. \frac{\partial V(r, R)/\partial R}{V(r, R)} \right|_{R=R_0} \times (R - R_0) \right\} \quad (5b)$$

$$\approx V_1(r) e^{\alpha(R-R_0)} \quad (6)$$

where

$$\alpha = \left. \frac{dV(r_e, R)/dR}{V(r_e, R)} \right|_{R=R_0};$$

r_e is distance of closest approach, R_0 is equilibrium bond distance.

It should be noted that the α in eqs. (5) and (6) is equal in magnitude to A_p as derived in ref. [5] but differs in sign.

However, a change of sign does not affect the matrix elements (3), when harmonic oscillator functions are used, as they are even in A_p ; this is not so in the present computation, and the sign of our α is the same as that in the expression quoted by Takayanagi [9].

Calculations were carried out over a large number of partial waves and for different values of the projectile collision energy E_{coll} ; more than 600 partial waves had to be included to obtain total cross sections for E_{coll} values greater than 5 eV.

A varying number of vibrational states (open channels only) was considered in the close-coupling procedures in order to test cross section convergence as compared with previous results [5].

3. DISCUSSION

The evidence from resonance emission spectroscopy indicates that the excitation of more than one vibrational quantum per collision is an extremely improbable process [10], and though a high probability attends the production of high vibrational levels from those immediately below, this restriction on Δv indicates the stepwise nature of the overall excitation. The very low probabilities of collisional excitation of lowest vibrational levels, evidenced from absorption and dispersion of high-frequency sound waves, may well be rate-controlling in the complete process.

This is why we have focussed our attention on the Q_{0-1}^{tot} total cross section, in the translational energy range corresponding to temperatures ranging between 100 and 4000°K. The results are listed in table 1 and compared with the corresponding harmonic oscillator results.

It has also been verified that the Q_{01}^{tot} cross sections remain unaltered if more than the 5 lowest vibrational levels are coupled together,

* The normalization constant produced in ref. [8] is correct although defined slightly differently. It disagrees with ref. [7].

Table 1
Total cross sections for collision induced vibrational excitation in carbon monoxide

Collision energy (eV)	Collision cross sections (πa_0^2 units) *	
	A	B
0.50	$2.00 \cdot 10^{-9}$	$2.01 \cdot 10^{-9}$
1.50	$0.120 \cdot 10^{-1}$	$0.027 \cdot 10^{-7}$
2.00	$0.80 \cdot 10^{-1}$	$0.170 \cdot 10^{-1}$
2.50	0.220	0.0680
3.50	1.203	0.344

A = harmonic oscillator model.

B = Morse oscillator model.

* Five vibrational levels were coupled together in all cases, except for $E_{\text{coll}} = 0.5$ eV, where only two levels were considered

showing therefore the same convergence behaviour as was exhibited previously by the harmonic oscillator model [5].

The empirical parameters relative to the potential of eq. (1) were obtained from spectroscopic data recently listed for several diatomic molecules [11].

It appears from the present results that the anharmonicity effect does not alter the lowest inelastic cross section by an order of magnitude. It is, however, of interest that the overall effect goes towards lowering the Q_{01}^{rot} 's by a factor of 3 or 4, and that such a reduction diminishes with the increasing collision energies (table 1). A similar behaviour was also found for the parameter variations of the (6-12) interaction potential [5]. Moreover, if the vibrational relaxation time τ for a gas in translational equilibrium is given by $1/\tau = \gamma_{10} - \gamma_{01}$, as described by Herzfeld and Litowitz [12], our lower values for the Q_{01} cross section bring the calculated τ 's into better agreement with experimental findings for carbon monoxide than did the h.o. case results (see fig 1 in ref. [5]).

Fig. 1 shows the cross section dependence upon the collision energy of the incoming projectile for both the approximations employed to describe the vibrational wavefunctions: at higher energies the anharmonicity effects seem to show a greater departure from the simple harmonic oscillator model, but at even higher energy values the dependence is inverted.

It is our opinion, however, that a better understanding of gas collisional activation processes requires a more "a priori" evaluation of the interaction potential at short and long ranges and necessitates a more explicit introduction of

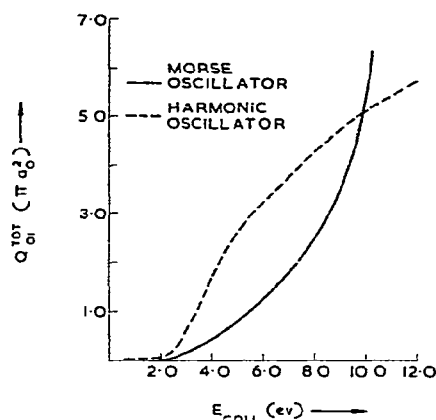


Fig. 1. Cross section for 0-1 vibrational excitation of CO by CO.

its angular dependence. Studies in this direction are being carried out at present [13].

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