



Observation of an odd/even deltaJ propensity in the collisional excitation of CO2 by hot deuterium atoms

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composition dependence of this thermodynamic chi parameter to be in good agreement with the estimates given by Sariban *et al.*¹³ based on Monte Carlo simulations of short lattice chains.

In contrast to the relative composition dependence of χ_s , we find that its actual value depends strongly on N. In particular, the calculated χ_s is significantly smaller than the mean field or "bare" $\chi_0 [2\rho^{-1} \chi_0 k_B T = \hat{v}_{AA} (0) + \hat{v}_{BB} (0)$ $-2v_{AB}(0)$] expected in the absence of any correlations. Bates and Wignall⁶ found from SANS measurements that $\chi_s \approx \chi_0$, where, χ_0 was estimated from a continuum cavity model utilizing C-H and C-D bond polarizibilities. The recent theoretical treatment of Bates and co-workers⁷ also predicts that $\chi_s \approx \chi_0$ by fitting the theory to the experimental composition curves, however, it should be pointed out that unlike the present approach, the theory of Bates et al.7 displays an unphysical divergence⁷ at the wings ($\phi = 0$ and 1). Sariban and co-workers,¹¹⁻¹³ on the basis of Monte Carlo calculations on a simple cubic lattice, found that $\chi = \chi_0/2.5$ for N = 32 at the spinodal. We calculate that for an equivalent Gaussian chain in continuous space that $\chi_s \approx \chi_0/8$. Thus our RISM calculations indicate that the calculated γ_s is "renormalized" downward from the bare χ_0 , thereby stabilizing the miscible region. In fact, we find that for large N, the renormalization effect increases such that $\chi_s/\chi_0 \propto 1/$ \sqrt{N} . This behavior suggests that the attractive interactions induce correlations in the blend which give rise to an extra entropic term in the free energy of mixing in continuous space. The magnitude of this renormalization of chi is expected to depend on the details of the intramolecular structure and the specific shape of the attractive potential. The qualitative trends stated here, however, are primarily due to off-lattice effects and are expected to be general for flexible polymer blends. The details of the calculations and additional results will be published in a future paper.²⁴

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Observation of an odd/even delta-J propensity in the collisional excitation of CO₂ by hot deuterium atoms

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Quantum state resolved studies of collisional energy transfer between translational and internal degrees of freedom are of considerable interest.¹⁻¹¹ Vibrational close couple-infinite order sudden calculations by Alexander and Clary^{12,13} on He–CO₂ collisions have shown interesting oscillations in cross sections as a function of rotational quantum number for excitation into states involving nonzero vibrational angular momentum. This effect has been attributed to symmetries in the 3-*j* coefficients of the carbon dioxide wave function. We report here the first experimental observation of such oscillations in the rovibrational excitation of CO_2 (01¹0) by hot atoms. Similar phenomena have been observed for collisions involving CN radicals¹⁴ and the photodissociation of ozone to give O_2 molecules,¹⁵ but we

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believe this is the first case in which these oscillations have been detected in a triatomic molecule.

The diode laser absorption probe technique has been described previously.^{7,8,11} Briefly, hot hydrogen or deuterium atoms are produced by the excimer laser photolysis of H_2S or D_2S at 193 nm:

$$D_2S + hv(193 \text{ nm}) \rightarrow DS + D^*$$
 ($E_{\text{trans}} = 2.16 \text{ eV}$),

$$H_2S + h\nu(193 \text{ nm}) \rightarrow HS + H^* \quad (E_{trans} = 2.30 \text{ eV}).$$

Collisions with CO_2 cause rotational and vibrational excitation:

$$D^* + CO_2(00^00; J') \rightarrow D + CO_2(mn^1p; J)$$
.

A tunable diode laser probes CO_2 molecules via absorption in the strongly allowed v_3 band:

$$CO_2(mn^1p; J) + h\nu(\sim 4.3 \ \mu m) \rightarrow CO_2(mn^1p + 1; J - 1)$$
.

Tunable diode radiation was passed through a 2 m sample cell collinearly with 193 nm excimer radiation. The diode was tuned to various rotational lines in the *P* branch of the $01^{1}1 \leftarrow 01^{1}0$ vibrational band of CO₂. A 1:1 mixture of D₂S and CO₂ at 25 mTorr flowed through the cell. Time-resolved changes in infrared absoption were detected by an InSb detector, amplified, and signal averaged on a digital oscilloscope.

A typical time-resolved signal displays a detector-limited fast rise (~ 600 ns) followed by a slow rise or decay. The time between CO₂/CO₂ or CO₂/D₂S collisions at 25 mTorr is $\sim 4 \mu s$, much slower than the detector response time. Thus the fast rise amplitude represents the nascent population produced by the hot D atom/CO₂ collision. The slow component of the signal is due to subsequent collisional relaxation. The fast rise amplitudes were normalized by excimer and diode laser powers to obtain the rotational distribution of the 01¹0 state, which is shown in Fig. 1. The most obvious feature in the distribution is that odd J levels have more population than even J levels. When the same experiment is performed with the absorption cell cooled to -50 °C, the populations of the even J levels are reduced, and the odd Jlevels are increased; thus the odd/even ratio increases at lower temperatures. Both pure rotational scattering (01¹0, $J \rightarrow 01^{10}$, J') and vibration-rotation scattering (00⁰0, $J'' \rightarrow 01^{10}$, J''') can, in principle, exhibit an odd/even scattering propensity.^{12,13} (The population of 01¹0 is 8% that of $00^{0}0$ at room temperature.) Nevertheless, the observed oscillation in the scattering process is apparently dominated by vibration-rotation scattering since the oscillation becomes larger as the sample is cooled, which significantly decreases the 01¹0 population. This is not surprising since the 01¹0 level has both even and odd initial J states, and averaging over the initial Boltzmann rotational distribution tends to obscure any delta-J propensity.^{12,13} For the dominant 00°0 molecules, however, only even J can exist, so a delta-J odd propensity is not averaged out. This implies that pure rotational scattering within the 01¹0 manifold is a relatively minor contributor to the observed distribution. Since only 8% of the CO₂ molecules are in the 01^{10} state at room temperature, the cross section for rovibrational excitation must be greater than about 10% of the cross section for pure rotational excitation.



FIG. 1. The rotational distribution of CO_2 in the 01¹0 vibrational state after collision with hot D atoms at 2.16 eV. Lines are shown connecting the data points for even J and for odd J in order to emphasize the difference between even and odd J. The room temperature Boltzmann distribution of CO_2 is peaked at J = 15.

A similar rotational distribution is observed for hot hydrogen atom scattering, although the total excitation probability into the v_2 manifold is smaller by a factor of about 0.7. The 01¹1 combination state, however, shows the opposite propensity in that the scattering probability into even Jstates is greater than into odd J states. This is due to the change in the wave function symmetry caused by the addition of a v_3 vibrational quantum.¹⁶ The 01¹1 propensity is clearly a vibration-rotation effect since the ambient population of 01¹1 is negligible under our experimental conditions.

Another feature of the 01^{10} distribution produced by hot D atom collisions is that it is peaked at about J = 43, significantly greater than the J = 31 peak for the $00^{0}1$ distribution.⁹⁻¹¹ This is most likely an indication of the effect of different trajectories on the efficiency of collisional excitation for the different vibrational modes. Quasiclassical calculations indicate¹⁷ that the v_3 stretch is excited roughly by end-on collisions, while broadside collisions play a more significant role in exciting the v_2 bend.

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NOTES

Theoretical characterization of a new *nd* Rydberg series of the *trans* 1,3 butadiene molecule

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In a recent experiment Taylor et al.¹ reinvestigated a previously assigned ns Rydberg series² for the trans-butadiene molecule, using multiphoton ionization spectroscopy with both linear and circularly polarized light. The polarization ratio Ω , defined as the ratio of the two-photon transition rate for excitation due to circularly polarized light to that for excitation due to linear polarized light, was measured for all the transitions observed in the region previously proposed for the ns Rydberg series. From their results, and based on some selection rules³ for Ω , Taylor *et al.* concluded that the previous assignment of an ns Rydberg series was not consistent with the measured values of Ω . On the other hand, the fact that the polarization ratio was always found to be less than 1 was consistent with an excited state of the same symmetry as the ground state (A_g) . Therefore, the authors reassigned the observed transitions to an nd_{π} Rydberg series.

In a previous study⁴ we have assigned the transitions calculated at 7.68 and 7.79 eV to the first members of the nd_{xy} and nd_{xz} Rydberg (nd_{π}) series, respectively. The calculation was limited to the first member of the series because the basis set was not adequate to describe the higher members. In this communication we present results of extensive MCSCF and CI calculations for several members of the nd_{xy} series. Besides the need of keeping the problem computationally tractable, we restricted the calculation to this series because the $3d_{xy}$ state of our previous work is in very good agreement with Taylor's¹ results. Also, the fact that the $3d_{xz}$ state has not been observed experimentally¹ suggests that the members of this series are less intense than the ones for the nd_{xy} series. A similar situation was found, both theoretically and experimentally, for the np_{σ} states of the butadiene molecule. In fact, even if the $3d_{xz}$ state was observed, a simple calculation based on the quantum defects for the two d_{π} series shows that, as the principal quantum number increases, the two series rapidly become degenerated, thus preventing the identification of the different components. For instance, the transition energies to the $4d_{xy}$ and $4d_{xz}$ states would differ by only 0.05 eV.

All the calculations were carried out using the Dunning⁵ valence double- ζ (DZ) contraction of the Huzinaga⁶ double- ζ Gaussian basis set augmented with diffuse basis functions of d_{π} character ($\zeta = 0.049$ and 0.015) on each carbon atom, in order to provide an adequate description of the Rydberg states. With the molecule in the yz plane, we

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