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State-to-state rotational excitation of CO by H₂ near 1000 cm⁻¹ collision energy

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Relative state-to-state rotationally inelastic cross sections for excitation of carbon monoxide by hydrogen were measured in a crossed molecular beam experiment at collision energies 795, 860, and 991 cm⁻¹. The results are compared to predictions of a recent *ab initio* potential energy surface [J. Chem. Phys. **108**, 3554 (1998)]. The agreement is very good. A comparison with older data on thermally averaged total depopulation cross sections [Chem. Phys. **53**, 165 (1980)] indicates that the absolute magnitudes of the cross sections predicted by the surface are too high. The CO excitation is dominated by collisions that are elastic in H₂ rotation, and the collision dynamics are very similar for different rotational levels of hydrogen. © 2000 American Institute of Physics.
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I. INTRODUCTION

The interaction of hydrogen and carbon monoxide is of interest for two main reasons. First, it serves as a prototype for molecule–molecule interactions with weak electrostatic components. Second, it is of practical importance to astrophysicists, who use CO emission and absorption as indicators of conditions in space; the CO state distributions they observe are strongly influenced by collisions with hydrogen.

This article presents molecular beam experiments on H₂–CO collisions. Previous experimental work can be divided into three classes: molecular beam studies, experiments on thermal gas mixtures, and spectroscopy of the H₂–CO van der Waals complex. Our review of earlier experimental work will follow that outline and will concentrate on rotational energy transfer. The literature on *vibrational* relaxation of CO by H₂ and its isotopomers was recently reviewed by Reid *et al.*¹

Several molecular beam experiments on H₂–CO collisions have been performed. Butz *et al.* measured total integral cross sections for collisions of CO with HD and D₂ in 1971,² and in 1973 Kupperman *et al.* measured elastic differential cross sections for H₂–CO scattering.³ Neither group detected angular dependence in the potential, and both extracted Lennard–Jones parameters; the two experiments gave consistent results. Andres *et al.* measured total differential cross sections and time-of-flight distributions in crossed supersonic beams of D₂ and CO in 1982.⁴ Their experiments did not show complete rotational resolution but rotational rainbow structures in the data gave information on the inelastic collisions.

Bréchnignac *et al.* performed an infrared–infrared double resonance experiment to determine state-to-state rate coefficients and velocity averaged rotationally inelastic cross sections for collisions of the $v=1$ state of CO with H₂.⁵ Several studies of CO pressure broadening by H₂ are

available.^{6–10} Schramm *et al.* determined interaction second virial coefficients for H₂–CO mixtures.¹¹

Kudian and Welsh first observed the spectrum of the *para*-H₂–CO van der Waals complex in the region of the H₂ stretching fundamental at high density (several amagats) in a low temperature cell.¹² This work was later extended by McKellar.¹³ The high density precluded resolution of individual rotational lines of the complex in either experiment. McKellar recently reported spectra in the CO stretch region that do not suffer that difficulty.^{14,15} Most of the observed lines of the *para*-H₂–CO spectrum have been assigned, but no analysis of the *ortho*-H₂–CO spectrum has appeared.

Theoretical interest in H₂–CO has been steady since the important 1976 article of Green and Thaddeus,¹⁶ who estimated state-to-state rates for H₂–CO collisions with a scaled He–CO potential surface. By 1984 four different H₂–CO potential surfaces had appeared.^{17–20} The ‘‘Hartree-Fock +damped dispersion’’ potential of Schinke *et al.*²⁰ was constructed with damping parameters chosen to fit the molecular beam data of Andres *et al.*⁴ Though it was later shown not to give good agreement with experimental second virial coefficients¹¹ or the van der Waals spectra,^{15,21} it was the best surface available until recently. Danby *et al.*²¹ computed bound levels on the surfaces of Flower *et al.*¹⁸ and Schinke *et al.*²⁰ and made a preliminary comparison to the infrared spectrum of H₂–CO. Parish *et al.*²² reported a ‘‘molecular mechanics for clusters’’ study, and Salazar *et al.*²³ reported high-level *ab initio* calculations for a limited number of nuclear configurations and included a good review of the theoretical work up to 1995.

In 1998 Jankowski and Szalewicz published a new four-dimensional surface that treated H₂ and CO as rigid rotors.²⁴ It was determined with symmetry-adapted perturbation theory (SAPT).²⁵ This new surface fared well in a comparison with the infrared *para*-H₂–CO spectrum of McKellar, and is the most accurate *ab initio* surface now available.

In this article we present measurements of relative state to state integral cross sections for rotational excitation of CO

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by hydrogen. The cross sections are sensitive to anisotropy in the repulsive wall of the interaction, and are nearly independent of the shape of the attractive well. They therefore provide a test of proposed potential surfaces that is complementary to that of the van der Waals spectra. We compare the experimental results with predictions of the Jankowski and Szalewicz surface.

II. EXPERIMENT

The details of our experimental apparatus and procedures have been described in earlier publications on CO scattering.^{26,27} Two pulsed, skimmed, supersonic molecular beams, one of neat H₂ and one of 5% CO seeded in Ar, intersected in a vacuum chamber. Relative densities of different rotational states of CO in the intersection volume were determined by resonance enhanced multiphoton ionization (REMPI).

A commercial pulsed valve of the current-loop design (R. M. Jordan) generated the hydrogen beam. Time-of-flight analysis with two fast ionization gauges (Beam Dynamics) showed that its most probable speed was 3110 ± 30 m/s, higher than would be expected from a room temperature source. We attribute the extra speed to warming of the valve faceplate and spring during operation to approximately 335 K. The CO/Ar beam was produced by a piezoelectric valve of the Proch and Trickl design;²⁸ the commonly used formulas²⁹ for a room temperature source predict its speed reliably. The collision energy in the center-of-mass frame could be varied by adjusting the intersection angle of the two molecular beams. We performed experiments with intersection angles of 93°, 107°, and 140°, giving center-of-mass mean collision energies of 795, 860, and 991 cm⁻¹.

A measurement of the rotational distribution of a small amount of CO seeded into the H₂ beam placed an upper bound of 11 K on its translational temperature. The H₂ velocity spread dominates the spread in collision energies, and the corresponding upper bound on the collision energy spread σ_E/E is 12%–13%. A more realistic estimate is $\sigma_E/E \approx 6\%$.

A YAG-pumped pulsed dye laser whose output was tripled in KDP and BBO crystals provided probe light near 215 nm. The scattered density in each final state was determined by REMPI through the *S* branch of the $E^1\Pi \leftarrow X^1\Sigma^+$ transition.³⁰ Differences between signals obtained with and without the H₂ beam gave the collision induced density in each final CO rotational level. For most final levels with $j_{CO} \geq 3$, the collision induced signal was much larger than the background.

III. CALCULATIONS

We carried out quantum scattering calculations on the Jankowski and Szalewicz potential surface²⁴ with the MOLSCAT program.³¹ The coupled states approximation for the scattering of two rigid rotors³² and the hybrid propagator of Alexander and Manolopolous³³ were used. The remainder of this section gives details of the calculations. In the description following, H₂ is molecule 1 and CO is molecule 2. We use Jankowski and Szalewicz' definitions of angles: θ_1

and θ_2 are the tilt angles of H₂ and CO with respect to the intermolecular axis, and ϕ is the dihedral angle. When $\theta_2 = 0$, the H₂ is closer to the oxygen atom.

During the scattering calculations, the four-dimensional potential surface must be expanded in a basis of angular functions at each radial distance *R*. MOLSCAT includes a mechanism (the "VRTP mechanism") for making this expansion by Gaussian quadrature at each step in the propagation. However, for the two-rigid-rotor case, a large number (of order 300) of potential evaluations corresponding to many triples of angles (θ_1, θ_2, ϕ) are required at each step in the propagation, though the same set of angular coordinates is used each time. A naive use of the VRTP mechanism therefore results in quite inefficient code. We modified the VRTP mechanism of MOLSCAT and the potential evaluation routine of Jankowski and Szalewicz to (i) perform the angular sums in Eqs. (13), (14), (15), and (17) of Ref. 24 for each (θ_1, θ_2, ϕ) triple at program initialization and store the results, and (ii) allow the remaining work that must be done at each *R* to vectorize efficiently. After this modification, evaluations of the potential contributed negligibly to the total run time, and the overall speed of the calculations increased by approximately a factor of 100.

The angular basis set used limits L1MAX=6 and L2MAX=10. The Gaussian quadratures for projection of the potential onto the angular basis used 7, 11, and 6 points for integration in θ_1 , θ_2 , and ϕ , respectively; the integration in θ_1 was reduced to 4 points by the homonuclear symmetry of H₂. The radial propagation used a stepsize parameter STEPS = 9, and the propagation was carried out to a maximum distance of 25 Å. All these values were chosen on the basis of convergence tests done at a total angular momentum of $15\hbar$. The partial wave sum terminated when the inelastic cross sections had converged to within 0.02 Å²; it typically included 50–60 partial waves.

The rotational basis sets included $j_{H_2} = 0$ and 2 for *para*-H₂ and $j_{H_2} = 1$ and 3 for *ortho*-H₂. All energetically open rotational levels of CO, and at least one closed level, were included at each energy; the highest rotational level used in any run was $j_{CO} = 29$. The resulting number of channels for the highest energy calculation was 286.

For each experimental collision energy, calculations were done at four different total energies, corresponding to the experimental collision energy plus the internal energy of H₂ for initial rotor levels from 0 to 3. In addition calculations at many more energies, but with only $j_{H_2} = 0$ in the rotational basis, were performed for the purpose of calculating Boltzmann-averaged cross sections as described below.

IV. RESULTS

The experimental results, arbitrarily normalized to set the average density at the lowest observed j_{CO} to 1 at each energy, are shown in Fig. 1. Each point in that figure is an individual observation (one scan over a single rotational line). The error bars in the figure give the standard deviations of the individual observations based on shot-to-shot fluctuations in the signals.

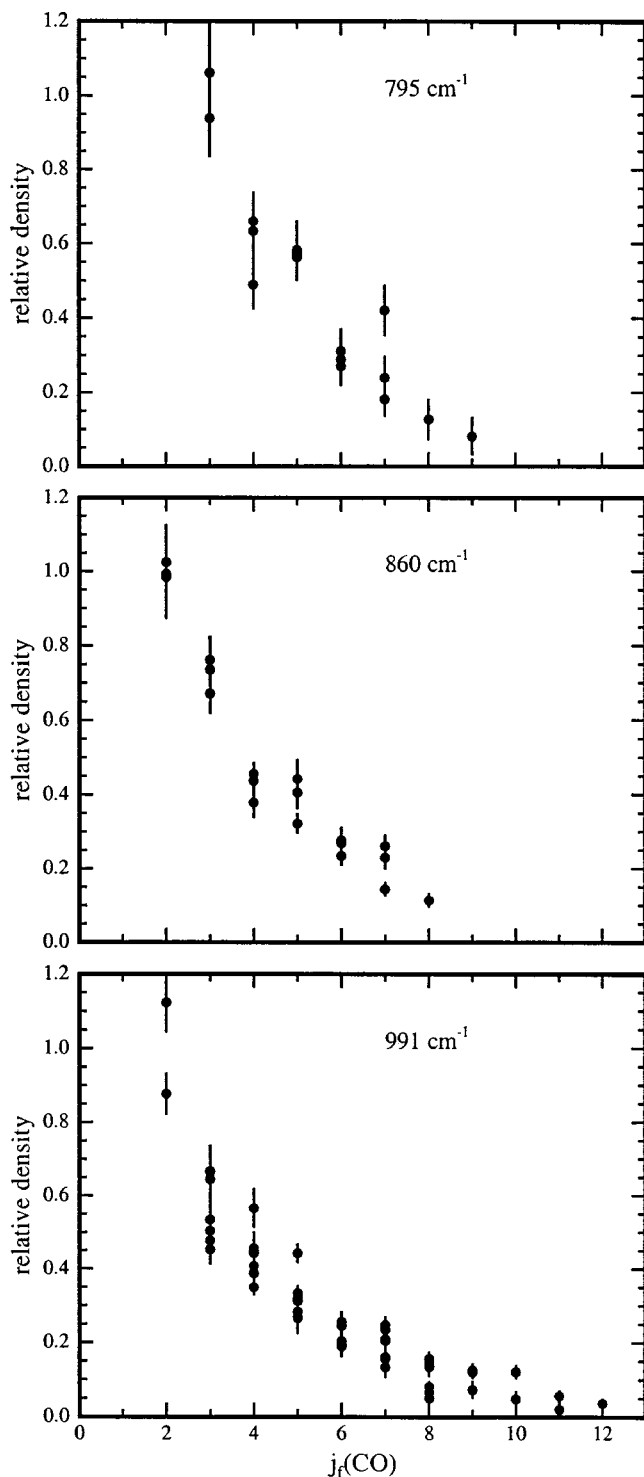


FIG. 1. Collision induced densities of final CO rotational levels. Duplicate points give results of independent measurements. Error bars give one standard deviation determined from shot-to-shot variations within each measurement. The vertical scales are separately normalized to 1 in the three panels.

From the theoretical state-to-state cross sections we constructed effective cross sections by averaging over the initial rotational distributions of H_2 and CO in the molecular beams and summing over the undetected final states of H_2 :

$$\sigma_{\text{eff}}(j) = \sum_{j_1=0}^3 \sum_{j_2=0}^1 f_{j_1}^{H_2} f_{j_2}^{CO} [\sigma(j_1, j_2 \rightarrow j_1, j) + \sigma(j_1, j_2 \rightarrow j_1 \pm 2, j)],$$

where j_1 represents the initial rotational state of H_2 and j_2 that of CO.

We determined the initial state distribution of CO each day during the experiments, and always found fractional populations in $j_{CO}=0$ between 0.7 and 0.8, with almost all the rest of the molecules in $j_{CO}=1$. We therefore took $f_0^{CO}=0.75$ and $f_1^{CO}=0.25$. We have no direct determination of the initial H_2 rotational distribution. However, two features of the calculated cross sections suggest that this ignorance is not important. First, the cross sections for collisions that are rotationally elastic in H_2 are typically 20–100 times larger than those that change j_{H_2} . Second, the rotationally elastic (in H_2) cross sections are nearly independent of the initial j_{H_2} . The effective cross sections were therefore independent of the initial rotational distribution of H_2 . We have made our comparisons with an assumed H_2 rotational temperature of 335 K, but identical conclusions would be reached with an assumed 0 K distribution.

The theoretical cross sections are superimposed on the experimental data in Fig. 2. In that figure, each experimental point represents the weighted mean of the corresponding points in Fig. 1, and the error bar gives two standard deviations in the mean [these quantities are defined by Eqs. (4.17) and (4.19) of Bevington and Robinson].³⁴ The error bars should be regarded as optimistic, since the reproducibility errors apparent in Fig. 1 may not be well described by a normal distribution. In each panel, a single scaling factor has been used to set the sum of the experimental cross sections for $3 \leq j \leq 9$ equal to the corresponding sum of theoretical effective cross sections. Table I lists the experimental data.

V. DISCUSSION

A. Possible systematic errors in experiments and calculations

The conversion of experimental signals to populations of CO final rotational states ignored several systematic effects. Probably the most important of these is the possibility of angular momentum polarization, since we made measurements only on the S branch of the transition and only with one laser polarization. We discussed the importance of polarization effects in our earlier article on He–CO scattering; in the present case, the most likely polarization would cause an underestimation of the populations in the higher rotational states on the order of 5%. The effect is therefore smaller than the experimental uncertainties.

We have also ignored the effect of the density-to-flux transformation, which makes our experiment more sensitive to CO molecules that move slowly in the laboratory. H_2 is much lighter than the CO molecule being probed. The variation in final CO speeds is therefore quite small, and no density-to-flux correction is necessary.

Two important approximations made in the calculations are the use of the coupled states approximation and the truncation of the rotational basis set to two H_2 levels. We expect the coupled states approximation to be quite good, because the scattering energy is on the order of ten times the van der Waals well depth. As a further check, we compared integral cross sections for $0 \rightarrow j$ transitions computed with both full

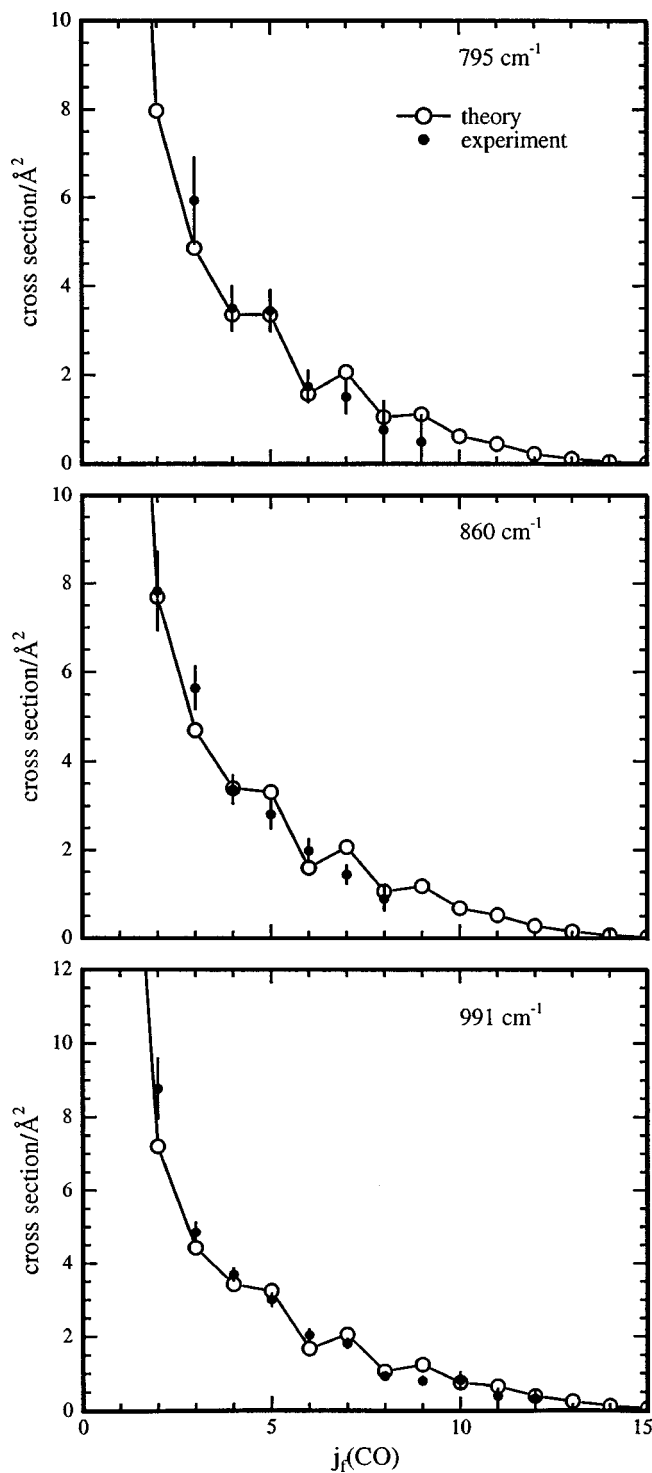


FIG. 2. Comparison of experimental collision induced densities with predictions of the SAPT surface (Ref. 24). Experimental error bars give 2σ in the weighted means of the measurements; see text for discussion.

close-coupled (CC) and coupled states (CS) methods, with only $j_{\text{H}_2}=0$ in the basis set, for a scattering energy of 100 cm⁻¹. In that comparison, the CS approximation gave integral cross sections within 3% of the CC ones except for the lowest-energy transition, $0 \rightarrow 1$, which is most influenced by long range forces, and the highest-energy transition, $0 \rightarrow 6$, which is near the energetic threshold. Those cross sections were overestimated in the CS calculations by 15% and 25%,

TABLE I. Experimental collision induced densities. Uncertainty figures give twice the estimated standard deviation in the mean, as in Fig. 2. Units are Å², determined by scaling the experimental data to the calculated cross-sections.

j_f	795 cm ⁻¹		860 cm ⁻¹		991 cm ⁻¹	
	n_f	2σ	n_f	2σ	n_f	2σ
2			7.82	0.89	8.77	0.82
3	5.93	0.98	5.64	0.47	4.85	0.25
4	3.50	0.50	3.37	0.31	3.69	0.17
5	3.44	0.46	2.81	0.31	3.00	0.17
6	1.74	0.35	1.98	0.26	2.04	0.14
7	1.50	0.37	1.44	0.20	1.82	0.12
8	0.76	0.64	0.89	0.26	0.93	0.10
9	0.49	0.59			0.81	0.11
10					0.82	0.22
11					0.40	0.18
12					0.332	0.19

respectively. In our experiments, the collision energy is much higher and no near-threshold transitions are observed. Both of those conditions should improve the accuracy of the CS calculations over our 100 cm⁻¹ test case.

We have included only the lowest two rotational states of H₂ in our rotational basis sets. Additional (mostly closed) rotational levels might make important contributions if they can become ‘‘temporarily populated’’ during scattering in the attractive part of the potential. However, the well depth is small compared to even the smallest H₂ rotational level spacing, and the potential does not have strong anisotropy in θ_1 , so we do not expect the missing channels to introduce much error.

The $j_{\text{H}_2}=2 \rightarrow 4$ transition is energetically allowed in the 860 and 991 cm⁻¹ experiments. The $2 \rightarrow 0$ cross sections are about 100 times smaller than the rotationally elastic ones, so we do not expect the $2 \rightarrow 4$ cross sections to make any detectable contribution.

B. Comparison between theory and experiment

1. State-to-state cross sections

Information about the potential surface is contained in two features of the relative inelastic cross-section data: the rate of fall of the cross sections with increasing j , and the interference structure that appears in the rotational populations. The falloff rate is determined by the overall anisotropy of the surface and the reduced mass, and is reproduced very well by the calculations. This feature is not particularly sensitive to details of the potential surface.

Interference between classical trajectories with different initial orientations of CO but the same classical angular momentum transfer can produce oscillations in the final rotational distributions of CO, as explained by Brumer³⁵ and by McCurdy and Miller.³⁶ The structure appears as clear oscillations in our work on CO excitation by rare gases,^{26,27} and in experiments on CN (Refs. 37–40) and NO (Refs. 4, 41–43) as well. Here, it is more subdued, and appears only as a steplike decrease: there is a large drop in the cross section from $j_f=3$ to 4, little change from 4 to 5, a large drop from 5 to 6, little change from 6 to 7, and so on. The structure is

more pronounced in the computed cross sections, with local maxima at $j_f=7$ and 9. The difference in amplitudes of the oscillations between experiment and theory is not sufficient to claim any real disagreement. (That difference is apparently not produced by the distribution of collision energies in the experiment: the depths of the oscillations in theoretical cross sections in the three panels of Fig. 2 are very similar, and those calculations were done at energies that differ by more than the experimental collision energy spread.) At any rate, it is clear that the calculation gets the phase of the oscillations right: odd Δj is preferred. This preference is the same one we observed in He–CO scattering,²⁶ and also appears in calculations on the earlier H₂–CO potential of Schinke *et al.* at 75 and 200 meV.⁴⁴

2. Thermally averaged total inelastic cross sections

Our experiments provide only relative, not absolute, values of the integral cross sections. Some information on the absolute cross sections is available from the state-to-state measurements of Bréchnignac *et al.*⁵ They measured relaxation rates of specific rotational states of CO ($v=1$) in an H₂ bath at 77 and 293 K with a time resolved IR–IR double resonance experiment. They extracted both thermally averaged total inelastic cross sections out of rotational states $j=9$ and 10, and a few kinetic parameters that characterized a large matrix of state-to-state rate coefficients.

To help determine whether the Jankowski and Szalewicz potential surface predicts the correct absolute magnitudes of cross sections, we have evaluated the total inelastic cross-section out of $j_{CO}=10$ for comparison with the 293 K result of Bréchnignac *et al.*⁵ We performed a Boltzmann average over kinetic energies, using trapezoidal rule quadrature at energies below 200 cm⁻¹ and Gauss–Laguerre quadrature at higher energies. The calculations for this average included only the rotationless level of H₂ in the basis set; they used the CS approximation above 100 cm⁻¹ but full CC calculations at lower energy.

The predicted total inelastic (depopulation) cross section out of $j_{CO}=10$ is 27.0 Å². The experimental value is 19.3 ± 3.7 Å², so the calculated cross section disagrees by about twice the stated experimental uncertainty. It is not clear from the article of Bréchnignac *et al.* whether that uncertainty is a simple statistical standard deviation, in which case a 2σ disagreement is not necessarily worrisome, or whether it includes an estimate of likely systematic error at a higher confidence level. Bréchnignac *et al.* obtained the experimental cross sections by monitoring the decay in population of a single rotational level in $v=1$ of CO, and their analysis neglected repopulation of this level by subsequent collisions. This neglect will produce an underestimate of the total inelastic cross section, and if that effect is not included in their error bars it may be contributing to the disagreement.

Error from the numerical quadrature probably does not exceed 1 Å², though the restricted basis set and the use of CS calculations introduce a larger uncertainty in the comparison with experiment. The exclusion of higher rotational states of H₂ in the calculation is more likely to cause an underestimate than an overestimate, so the disagreement is probably not from that source. The experiments used CO ($v=1$) while the

theoretical surface has the CO distance set at the average value for its ground vibrational state; this difference probably does not contribute a large error either.

Studies of second virial coefficients⁴⁵ and further work on H₂–CO spectra⁴⁶ indicate that the SAPT potential well is too deep by about 5%. That error would be expected to produce an overestimate of the 293 K inelastic cross sections, but since the average collision energy at that temperature is about twice the well depth it would be surprising if the effect were as large as 30%. A full explanation of the disagreement between measured and calculated cross sections is therefore not clear, but it is very likely that the SAPT potential overestimates the absolute cross sections by at least a few percent.

C. Similarity of *para* and *ortho* H₂

In the calculations, the dominant scattering processes are elastic in the H₂ rotation. For those, the cross sections for transitions into the different CO final states are remarkably independent of the H₂ rotational state. In other words, the rotational excitation of CO is not affected by the rotational state of the H₂ collision partner at the collision energies we have studied. One possible explanation rests on a simple classical idea: if the rotational period of H₂ in the low rotational levels is short compared to the collision time, the effects of different H₂ orientations will be averaged away. However, at 1000 cm⁻¹ the time spent on the repulsive wall during a typical collision is about 50 fs, while the classical rotational period of H₂ ($j=1$) is 200 fs. Therefore the averaging argument is not valid for low j_{H_2} . The insensitivity of the cross sections to H₂ rotational state must be due to small anisotropy of the potential in the θ_1 coordinate in the repulsive region.

VI. CONCLUSION

Experimental relative state-to-state cross sections for rotational excitation of CO by hydrogen agree with predictions of the Jankowski and Szalewicz potential surface. This agreement indicates that the shape of the repulsive wall on the theoretical surface is accurate. The surface agrees less well with absolute thermally averaged total inelastic cross-sections measured by Bréchnignac *et al.*; it appears to overestimate the total inelasticity modestly. Scattering calculations showed that rotationally inelastic cross sections are nearly independent of H₂ initial rotational state at collision energies near 1000 cm⁻¹.

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