

LETTER TO THE EDITOR

Low energy H+CO scattering revisited: CO rotational excitation with new potential surfaces

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ABSTRACT

Context. A recent modeling study of brightness ratios for CO rotational transitions in gas typical of the diffuse ISM by Liszt found the role of H collisions to be more important than previously assumed. This conclusion was based on recent quantum scattering calculations using the so-called WKS potential energy surface (PES) which reported a large cross section for the important $0 \rightarrow 1$ rotational transition. This result is in contradiction to one obtained using the earlier “BBH” PES for which the cross section is quite small and which is consistent with an expected homonuclear-like propensity for even ΔJ transitions.

Aims. To revisit this contradiction with new scattering calculations using two new ab initio PESs that focus on the important long-range behavior and to explore the validity of the apparent departure from the expected even ΔJ propensity in H-CO rotational excitation obtained with the WKS PES.

Methods. Close-coupling (CC) rigid-rotor calculations for CO($v = 0, J = 0$) excitation by H are performed on four different PESs. Two of the PESs are obtained in this work using state-of-the-art quantum chemistry techniques at the CCSD(T) and MRCI levels of theory.

Results. Cross sections for the $J = 0 \rightarrow 1$, as well as other odd ΔJ , transitions are significantly suppressed compared to even ΔJ transitions in thermal energy CC calculations using the CCSD(T) and MRCI surfaces. This is consistent with the expected even ΔJ propensity and in contrast to CC calculations using the WKS PES which predict a dominating $0 \rightarrow 1$ transition.

Conclusions. Inelastic collision cross section calculations are sensitive to fine details in the anisotropic components of the PES and its long-range behavior. The current results obtained with new surfaces for H-CO scattering suggest that the original astrophysical assumption that excitation of CO by H₂ dominates the kinetics of CO in diffuse ISM gas is likely to remain valid.

Key words. molecular processes – ISM: molecules

1. Introduction

Carbon monoxide is found in a variety of astrophysical environments usually being the most abundant molecule with the exception of H₂. It is typically observed in absorption in the UV and near-IR and in emission in the far-IR to millimeter wavelengths. For example, the *Infrared Space Observatory (ISO)* detected a large number CO rovibrational lines toward Orion Peak 1 and 2 (González-Alfonzo et al. 2002) while pure rotational lines were observed in the planetary nebulae NGC 7027 (Cernicharo et al. 1997).

In most environments, the molecular level populations are not in equilibrium, so that predicting spectral line intensities depends crucially on the magnitude of collisional excitation rate coefficients due to the dominant species H₂, He, and H. Adopting semiempirical potentials, Green & Thaddeus (1976) performed one of the earliest quantal scattering calculations for the CO-

H₂, CO-He, and CO-H systems at astrophysically relevant temperatures. Their results suggested that the rate coefficients for atomic hydrogen collisions were significantly less than those due to H₂, so that CO-H collisions were usually neglected in modeling studies of CO spectra.

The H-CO complex has been extensively studied by the chemical physics community for the past three decades including early ab initio PES calculations by Botschwina (1974). A later ab initio PES by Bowman, Bittman, and Harding (1986, BBH) was constructed and used in subsequent scattering calculations (Lee & Bowman 1987). The H+CO system has a barrier to the formation of the HCO complex at a H-CO internuclear separation of $4.2 a_0$ with a calculated height of 0.125-0.17 eV, but measured to be 0.087(17) eV ($\sim 700 \text{ cm}^{-1}$ or 1000 K) (Wang et al. 1973). Lee & Bowman (1987) found that for collision energies below the barrier, and not coincident with tunneling resonances, rotational excitation cross sections displayed

an even ΔJ propensity, i.e. homonuclear-like behavior at long-range.

Another H-CO surface was computed at the MRCI level of theory by Keller et al. (1996), the so-called WKS PES. This PES was found to reproduce H-CO spectroscopic measurements better than that of the BBH surface. It was also noted by Green et al. (1996) that the WKS and BBH surfaces gave different rotational excitation cross sections with the difference being most significant for the $0 \rightarrow 1$ transition. This discrepancy was ascribed to the differences in the treatment of the long-range portion of the potentials. Balakrishnan, Yan, & Dalgarno (2002) later confirmed this difference in the rotational excitation cross sections and therefore utilized the WKS surface for large-scale calculations of rotational excitation rate coefficients for astrophysical modeling applications.

Recently, Liszt (2006) adopted the new CO-H rotational excitation rate coefficients of Balakrishnan et al. (2002) in an investigation of the non-equilibrium rotational populations of CO in environments typical of the diffuse interstellar medium (ISM). He concluded that the increase in the rotational excitation rate coefficients for CO-H substantially enhanced CO rotational brightness and excitation temperatures and that CO-H collisions should not be neglected in future models.

However, what has been previously overlooked is that the new large $0 \rightarrow 1$ rate coefficient results in a departure from the homonuclear-like even ΔJ propensity which has been argued on reasonable physical grounds to be valid for the H-CO collision system (Lee & Bowman 1987). As the scattering results have been confirmed in a number of theoretical investigations, a possible explanation is a subtle deficiency in the long-range portion of the WKS surface. In this letter, we explore this issue by computing two new and completely independent H-CO rigid-rotor surfaces and performing close-coupling calculations to obtain the rotational excitation cross sections. We briefly describe the potential surface computations and scattering calculation methods in the next two sections. The results and their astrophysical implications are presented in Section 4 followed by a conclusion in Section 5.

2. Potential Energy Surface Calculations

One of the two new ab initio surfaces was calculated using the coupled cluster method with single and double excitations and a perturbative treatment of triple excitations [CCSD(T)] employing the frozen core approximation (Purvis & Bartlett 1982, Raghavachari et al. 1989). For the open-shell calculations, restricted open-shell Hartree-Fock orbitals were used in the CCSD(T) calculations, but the spin-restrictions were relaxed in the solution of the coupled cluster equations [R/UCCSD(T)] (Knowles et al. 1994). We adopted the doubly augmented correlation consistent d-aug-cc-pVnZ ($n = T, Q,$ and 5) basis set of Woon & Dunning (1994). The full counterpoise correction was applied to approximately account for basis set superposition error (Boys & Bernardi 1970). At each configuration, calculations were performed with all three basis sets for the dimer (HCO) and monomers (CO and H) and these energies were extrapolated to the complete basis set (CBS) limit. These extrapolated total energies were then used to compute the CBS limit counterpoise corrected interaction energies. The interaction potential was computed in Jacobi coordinates with the CO bond length r fixed at its experimental equilibrium value ($2.1322 a_0$) (Huber & Herzberg 1979). The resulting rigid-rotor PES that is a func-

tion of R (distance between H and the CO center of mass) and θ (angle between the vectors \mathbf{r} and \mathbf{R}) was fit to the expression

$$V(R, \theta) = \sum_{\lambda=0}^N P_{\lambda}(\cos \theta) V_{\lambda}(R) \quad (1)$$

where the P_{λ} are normalized Legendre polynomials with $N = 12$. The $V_{\lambda}(R)$ were calculated using 12th-order Gauss-Legendre quadrature. The two-dimensional grid on which the ab initio calculations were carried out corresponded to 23 values of R between $3-20 a_0$ and the 12 values of θ were obtained from the 12 Gauss-Legendre quadrature points. The large range in R was chosen in order to obtain good coverage of the long-range interaction, which is important in the low-energy scattering, as discussed below. The calculations were carried out with the MOLPRO suite of ab initio programs (Amos et al. 2002).

The second PES was computed using the complete active space self-consistent field [CASSCF] (Werner & Knowles 1982, Knowles & Werner 1985) and internally contracted multireference configuration interaction [MRCI] (Knowles & Werner 1988, 1992, Werner & Knowles 1989) method with aug-cc-pVQZ basis set for H, C, and O by Woon & Dunning (1994) as implemented in the MOLPRO program. Calculations were performed for $1-3 {}^1A'$ states in the C_s point group for all non-linear approaches in Jacobi coordinates, and for a CO bond length of $r = 2.20 a_0$. The rigid rotor PES was obtained for the following grid of points: $R = 1.6-5.0$ (0.2), $5.0-5.8$ (0.4), and $6.0-15.0 a_0$ ($1.0 a_0$) and $\theta = 1-179^\circ$ (15°), where the numbers in parentheses indicate the step-sizes for the corresponding range and coordinate. The final energies incorporate the Davidson correction (1974). The computed potential energy values were combined with an accurate ab initio long-range potential that includes C_6 , C_7 , and C_8 coefficients for the H-CO interaction. These coefficients have been obtained using Padé approximants with Cauchy moments evaluated by linear response coupled cluster (LR-CCSD) theory (Hättig et al. 1997) with the d-aug-cc-pwCV5Z basis set (Peterson & Dunning 2002) and correlating all 14 electrons of CO in the CCSD calculation. The long range part has been smoothly joined to the ab-initio calculated points and a full analytical representation of the rigid rotor potential with accurate long-range interaction was constructed and used in the scattering calculations.

3. Collisional Excitation Calculations

In the present study, the quantum close-coupling (CC) method (Arthurs & Dalgarno 1960, Lester 1971, Secrest 1979) was used for the calculations of rotational excitation due to H atom impact. CO was treated in the rigid-rotor approximation being held fixed at its equilibrium bond-length. The CC scattering calculations were performed by expanding the angular dependence of the relevant potential in Legendre polynomials as given in Eq. (1). Calculations were performed with the non-reactive molecular scattering program MOLSCAT (Hutson & Green 1994) to generate integral state-to-state cross sections. The CC equations were integrated using the modified log-derivative Airy propagator of Alexander and Manolopoulos (1987) with a variable step-size. A sufficient number of total angular momentum partial waves and basis set terms have been included to secure convergence of the cross sections.

4. Results and Discussion

Figure 1a compares the first four terms ($\lambda = 0 - 3$) of the Legendre expansion for the BBH and WKS surfaces as well as the new PESs computed in the current work, referred to as CCSD(T) and MRCI. The agreement between all surfaces appears to be reasonable at the scale of the figure. However, focusing on the long-range portion, clear differences are apparent in the $\lambda = 1$ component as shown in Fig. 1b. The present PESs are believed to be more reliable than previous surfaces because we have specifically focused on the long-range behavior through explicit calculations at much larger internuclear distances than in the earlier work. Further, the importance of the long-range behavior and its influence on low-energy collisions is elevated due to the barrier at $R = 4.2 a_0$ as described below.

Calculations of state-to-state cross sections from initial rotational state $J = 0$ for the excitation of CO by H on the MRCI, CCSD(T), BBH, and WKS surfaces were performed for collision energies at 400 and 800 cm^{-1} as given in Figs. 2 and 3, respectively. The cross sections using the BBH and WKS surfaces are in good agreement with those obtained by Green et al. (1995) and Balakrishnan et al. (2002), respectively. While the results presented here adopted the rigid-rotor approximation, we performed tests with BBH and WKS and found that the resulting cross sections using the full surfaces, i.e., with vibrational motion, are practically identical. The largest difference was less than $\sim 10\%$ for the $0 \rightarrow 1$ transition with WKS. Our rigid-rotor cross sections in Figs. 2 and 3 further confirm the previously noted result that the $0 \rightarrow 1$ transition using WKS is approximately an order of magnitude larger than that obtained with BBH.

Comparing now the rigid-rotor cross sections obtained with the new CCSD(T) and MRCI surfaces, we see that i) the two sets of cross sections are in very good agreement, ii) they reproduce the even ΔJ propensity obtained with BBH, and iii) the $0 \rightarrow 1$ transition is small with a value similar to that obtained with BBH, in contrast to the WKS result. These observations can be interpreted by examining the $\lambda = 1$ terms displayed in Fig. 1b since the dominant contributions to the state-to-state cross sections originate from potential coupling matrix elements with $\lambda = |\Delta J|$. The $\lambda = 1$ components from the CCSD(T) and MRCI calculations are seen to be very similar, both displaying a peak near $5 a_0$ and comparable long-range behavior. Conversely, for the WKS surface the $\lambda = 1$ component peaks at a shorter internuclear distance, closer to the barrier location, and has a different long-range behavior. Indeed, the long-range tail of the WKS potential appears to be decaying slower than the other potentials. The BBH $\lambda = 1$ component is smaller than that of the other surfaces which may explain its slightly smaller $0 \rightarrow 1$ cross section.

To further test the apparent discrepancy related to the $\lambda = 1$ component of the Legendre expansion, we examined scattering results for excitation of the $J = 1$ and 2 rotational states of CO ($v = 0$). The cross sections for the $\Delta J=1$ excitation transitions with the WKS surface were found to also be an order of magnitude larger than those obtained with the other surfaces.

Based on all of our scattering calculations in conjunction with the computation of the new surfaces, it appears that the WKS surface has a different anisotropic behavior, especially at long-range. This anisotropy, evident in the $\lambda = 1$ component, while of small magnitude, drives the $\Delta J = 1$ transitions and results in the significant discrepancy in the important $J = 0 \rightarrow 1$ cross section.

Our findings have important implications for modeling of CO in non-equilibrium situations, e.g. diffuse interstellar gas,

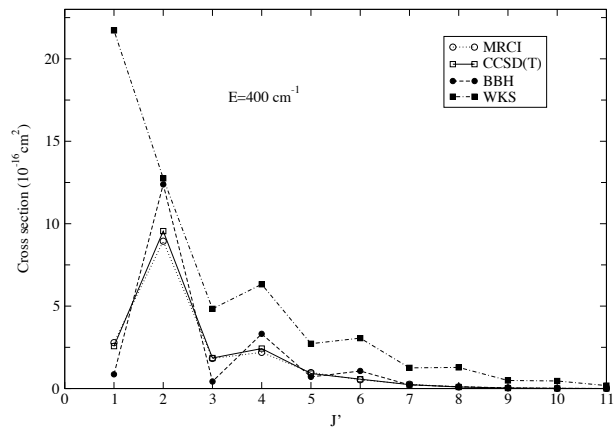


Fig. 2. Excitation cross sections due to H impact for CO ($v = 0, J = 0$) to CO ($v' = 0, J'$) for a center of mass collision energy of 400 cm^{-1} . Results obtained with different PESs are indicated by the symbols.

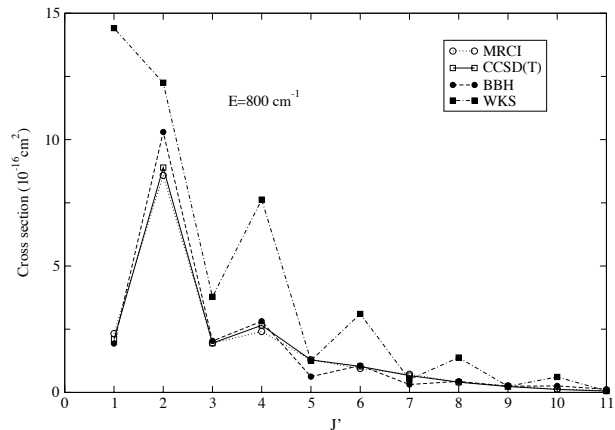


Fig. 3. Same as Fig. 2, but for a center of mass collision energy of 800 cm^{-1} .

where atomic hydrogen is present. The conclusions of Liszt (2006), based on the adoption of the rotational excitation rate coefficients obtained with WKS, that H collisions can significantly affect the CO rotational populations, and therefore modeling of the resulting absorption/emission lines, is no longer valid. In particular, the $0 \rightarrow 1$ cross section due to H impact is found to be much smaller than that due to H_2 collisions in agreement with the earlier results of Chu & Dalgarno (1975) and Green & Thaddeus (1976). Further, our results illustrate the sensitive dependence that low-energy scattering can have on fine details of the potential energy surface.

5. Conclusions

The current scattering calculations using the new CCSD(T) and MRCI surfaces have corroborated the expected even ΔJ propensity for the H-CO system at low collision energies. These findings indicate that the rotational excitation rate coefficients obtained in Balakrishnan et al. (2002) using the WKS surface are inaccurate bringing into question any astrophysical conclusions deduced from modeling with these rate coefficients. Instead of being large, the $J = 0 \rightarrow 1$ cross section is small as originally found by Chu & Dalgarno (1975). The supposition of Green & Thaddeus (1976) that excitation due to molecular hydrogen and He should dominate the non-equilibrium kinetics of CO remains valid. Calculations are currently underway to compute the full

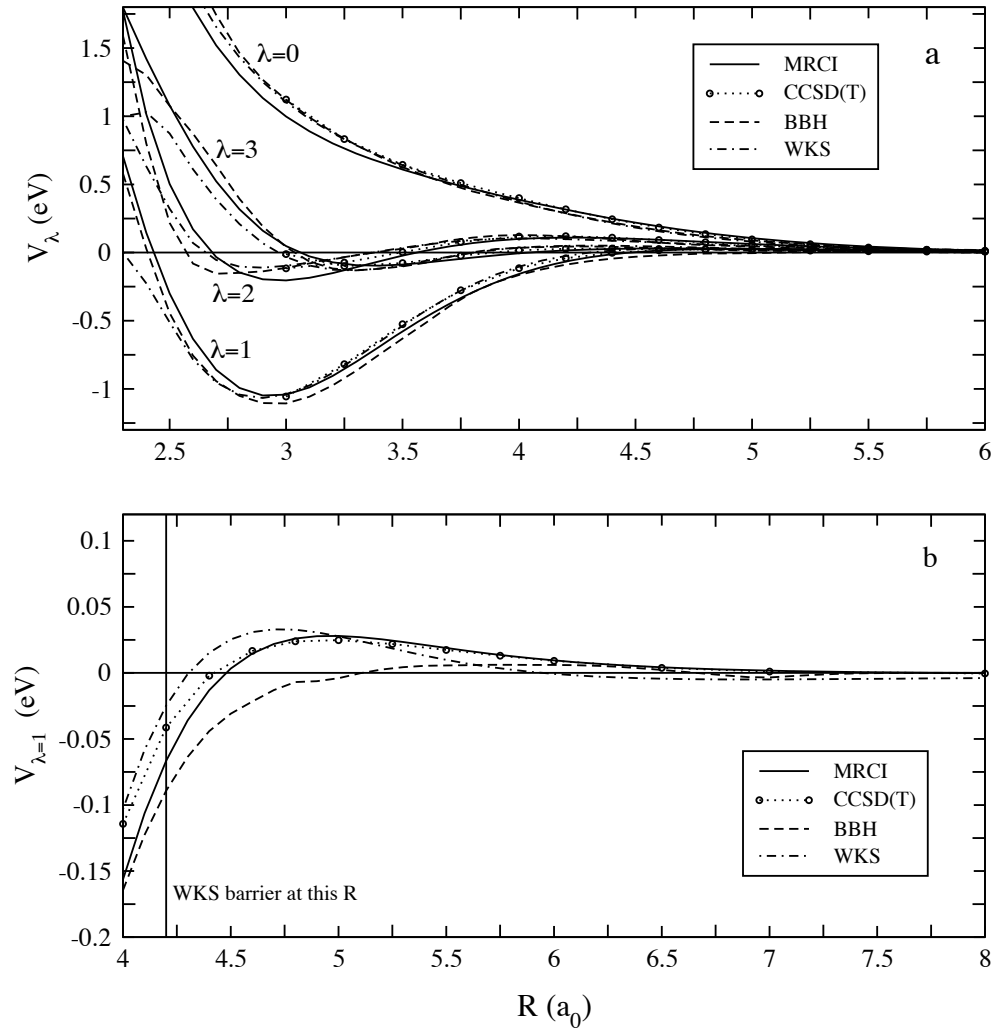


Fig. 1. (a) Legendre expansion terms $V_\lambda(R)$ for the H-CO PES with the CO internuclear distance r fixed at its equilibrium value. (b) Same as in (a), but focusing on the long-range behavior for $\lambda = 1$. See text for descriptions of the different surfaces.

long-range HCO surface at the CCSD(T) level which will allow for new large-scale scattering calculations for an extensive range of rotational and vibrational transitions.

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References

- Arthurs, A. & Dalgarno, A. 1960, Proc. Roy. Soc. London A, 256, 540
 Alexander, M. H. & Manolopoulos, D. E. 1987, J. Chem. Phys., 86, 2044
 Amos, A., Bernhardtsson, A., Berning, A., et al. 2002, MOLPRO is a package of ab initio programs written by H.-J. Werner and P.J. Knowles, version 2002.6, <http://www.molpro.net>
 Balakrishnan, N., Yan, M., & Dalgarno, A. 2002, ApJ, 568, 443
 Bowman, J. M., Bittman, J. S., & Harding, L. B. 1986, J. Chem. Phys., 85, 911 (BBH)
 Boys, S. F., & Bernardi, F. 1970, Mol. Phys., 19, 553
 Cernicharo, J., et al. 1997, ApJ, 483, L65
 Chu, S.-I. & Dalgarno, A. 1975, Roy. Soc. Lond. Proc. Ser. A, 342, 191
 González-Alfonso, E., Wright, C. M., Cernicharo, J., et al. 2002, A&A, 386, 1074
 Green, S. & Thaddeus, P. 1976, ApJ, 205, 766
 Green, S., Baiyu, P., & Bowman, J. M. 1995, J. Chem. Phys., 102, 8800
 Green, S., Keller, H.-M., Schinke, R., & Werner, H.-J. 1996, J. Chem. Phys., 105, 5416
 Hättig, C., Christiansen, O., & Jørgensen, P. 1997, J. Chem. Phys., 107, 10592
 Huber, K. P. & Herzberg, G. 1979, Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules. (Van Nostrand, Princeton)
 Hutson, J. M. & Green, S. 1994, MOLSCAT computer code, version 14, distributed by Collaborative Computational Project No. 6 of the Engineering and Physical Sciences Research Council (UK)
 Keller, H.-M., Floethmann, H., Dobbyn, A. J., et al. 1996, J. Chem. Phys., 105, 4983 (WKS)
 Knowles, P. J. & Werner, H.-J. 1985, Chem. Phys. Lett., 115, 259
 Knowles, P. J. & Werner, H.-J. 1988, Chem. Phys. Lett., 145, 514
 Knowles, P. J. & Werner, H.-J. 1992, Theor. Chim. Acta 84, 95
 Knowles, P. J., Hampel, C., & Werner, H.-J. 1994, J. Chem. Phys., 99, 5219
 Langhoff, S. R. & Davidson, E. R. 1974, Intl J. Quantum. Chem. 8, 61
 Lee, K.-T. & Bowman, J. M. 1987, J. Chem. Phys., 886, 215
 Lester, W. A., Jr. 1971, Meth. Comput. Phys., 10, 211
 Liszt, H. S. 2006, A&A, 458, 507
 Peterson, K. A. & Dunning, T. H., Jr. 2002, J. Chem. Phys., 117, 10548
 Purvis, G. D. I., & Bartlett, R. J. 1982, J. Chem. Phys., 76, 1910
 Raghavachari, K., Trucks, G. W., Pople, J. A., & Head-Gordon, M. 1989, Chem. Phys. Lett., 157, 479
 Secret, D. 1979, in Atom-Molecule Collision Theory: A Guide for the Experimentalist, edited by R. B. Bernstein (Plenum, New York)
 Wang, H. Y., Eyre, J. A., & Dorfman, L. M. 1973, J. Chem. Phys., 59, 5199
 Werner, H.-J. & Knowles, P. J. 1985, J. Chem. Phys., 82, 5053
 Werner, H.-J. & Knowles, P. J. 1989, J. Chem. Phys., 89, 5803
 Woon, D. E. & Dunning, T. H., Jr. 1994, J. Chem. Phys., 100, 2975