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Riccardo Conte, Paul L. Houston, and Joel M. Bowman

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## Communication: A benchmark-quality, full-dimensional *ab initio* potential energy surface for Ar-HOCO

Riccardo Conte,<sup>1,a)</sup> Paul L. Houston,<sup>2,b)</sup> and Joel M. Bowman<sup>1,a)</sup> <sup>1</sup>Department of Chemistry and Cherry L. Emerson Center for Scientific Calculation, Emory University, Atlanta, Georgia 30322, USA

<sup>2</sup>School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

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A full-dimensional, global *ab initio* potential energy surface (PES) for the Ar-HOCO system is presented. The PES consists of a previous intramolecular *ab initio* PES for HOCO [J. Li, C. Xie, J. Ma, Y. Wang, R. Dawes, D. Xie, J. M. Bowman, and H. Guo, J. Phys. Chem. A **116**, 5057 (2012)], plus a new permutationally invariant interaction potential based on fitting 12 432 UCCSD(T)-F12a/aVDZ counterpoise-corrected energies. The latter has a total rms fitting error of about 25 cm<sup>-1</sup> for fitted interaction energies up to roughly 12 000 cm<sup>-1</sup>. Two additional fits are presented. One is a novel very compact permutational invariant representation, which contains terms only involving the Ar-atom distances. The rms fitting error for this fit is 193 cm<sup>-1</sup>. The other fit is the widely used pairwise one. The pairwise fit to the entire data set has an rms fitting error of 427 cm<sup>-1</sup>. All of these potentials are used in preliminary classical trajectory calculations of energy transfer with a focus on comparisons with the results using the benchmark potential. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4871371]

Much attention has recently been drawn to the HOCO radical,  $^{1-3}$  an intermediate in the OH + CO  $\rightarrow$  H + CO<sub>2</sub> reaction which is important for conversion of CO to CO<sub>2</sub> in combustion<sup>4</sup> and atmospheric chemistry.<sup>5,6</sup> The presence of the HOCO intermediate has been experimentally inferred by means of thermal rate constant measurements<sup>7–9</sup> and molecular beam experiments<sup>10</sup> that have pointed out the reaction proceeds via formation of a HOCO complex.<sup>11,12</sup> The global potential energy surface is fairly complicated and contains two HOCO minima (the planar trans- and cis-isomers).<sup>13,14</sup> Photodetachment experiments of the HOCO<sup>-</sup> anion<sup>15-17</sup> have indicated tunneling from the HOCO wells to the  $H + CO_2$  products, an aspect highlighted also in recent calculations.<sup>18,19</sup> Further theoretical studies on the aforementioned reaction have been performed by means of quasi-classical trajectory and quantum dynamics calculations<sup>20,21</sup> based on recent ab initio global potential energy surfaces (PESs) obtained by means of permutationally invariant fits or neural networks. These global surfaces have outperformed previous work which had focused only on limited portions of the configuration space.<sup>22-30</sup>

Due to the intermediate nature of the HOCO radical, its stabilization is of importance in combustion modeling. Thus, it is interesting to perform simulations where the radical interacts with an inert gas. The collision leads to an energy transfer that can either stabilize the complex (and so increase its lifetime) or speed up the reaction. By using a standard procedure in energy transfer calculations, the intramolecular po-

a)Electronic addresses: riccardo.conte@emory.edu and jmbowma@emory.edu

b)Electronic mail: paul.houston@cos.gatech.edu

tential can be separated from the interaction one. The latter is usually approximated by means of a pairwise potential (see, for instance, Refs. 31–36). An alternative, but more expensive and not always feasible approach to treat the collision is represented by *ab initio* direct dynamics.<sup>37–39</sup>

In this Communication, we present an accurate, global *ab initio* full-dimensional PES obtained for the Ar-HOCO system. The PES is represented by the sum of a recent permutationally invariant (PI) *ab initio* intramolecular HOCO potential,<sup>20</sup> (other recent *ab initio* HOCO PESs<sup>13, 14</sup> could also be used, as well) plus a full-dimensional interaction PES, presented here. This PES is a precise PI fit to 12 432 *ab initio* energies.<sup>40</sup> Two additional fits are presented. One is a novel, compact PI representation, which contains terms only involving the Ar-atom distances. The other fit is the widely used pairwise one. These fits are used in classical trajectory calculations of energy transfer between argon and highly internally excited HOCO with the aim of comparing the results using the pairwise and compact PI fits to the benchmark PI one.

Permutationally invariant fitting of many thousands of electronic energies<sup>41</sup> has been successfully used for a large number of reactive molecular PESs. PI fitting has not, however, been used for non-covalent interactions, which govern energy transfer between an inert collider, such as Ar or N<sub>2</sub>, and an energized molecular complex. Such interactions have typically been approximated by semi-empirical pairwise potentials. We recently reported a pairwise potential for the Arallyl interaction where the parameters were obtained by (nonlinear) least-squares fits to several hundred *ab initio* electronic energies.<sup>36</sup> Because of the low order of the permutation group for Ar-HOCO we use simple symmetrized monomial PESs<sup>42</sup> for the fit to the interaction potential. Thus, the interaction

TABLE I. Comparison between the different fits. Number of coefficients to fit and rms errors ( in  $cm^{-1}$ ) for different energy regions (E in eV).

	Ncoeff	rmse (all energies)	rmse (E < 0)	rmse (0.0 < E < 0.5)	rmse (0.5 < E < 1.0)	rmse $(1.0 < E < 1.5)$	
Pairwise-18 18		427.5	66.0	378.6	1103.3	1846.2	
PI-79	79	193.4	31.6	232.2	552.5	678.8	
PI-1376	1376	24.6	12.8	32.9	57.2	70.5	

potential is written as

$$V_{inter} = \sum_{n_1 + \dots + n_{10} = 0}^{M} D_{n_1, \dots, n_{10}} \mathcal{S}[y_1^{n_1} \dots y_{10}^{n_{10}}].$$
(1)

S indicates the operator that symmetrizes the monomials  $(y_i = e^{-r_i/\alpha})$  where  $(r_i)$  is the *i*th internuclear distance and  $\alpha$  is a range parameter. A maximum order of monomials involved is chosen  $(M \ge n_1 + \ldots + n_{10})$ . In our case, HOCO-Ar is an  $A_2BCD$  system and we chose a maximum order M = 5. The total number of permutationally invariant polynomials thus obtained is 1632. The value M = 5 is high enough for a very accurate fit. Higher M values would have the drawbacks of an increased number of *ab initio* energies needed and a slower computational performance due to the larger number of polynomials to evaluate at every interaction potential calculation.

Two modifications were made to the general expression above for the present application. One was to eliminate terms that do not exactly vanish at large Ar distances from HOCO. Doing so results in a reduction in the total number of polynomials to 1376. The second modification was to use two range parameters,  $\alpha_2$  for all Ar-atom variables, and  $\alpha_1$  for all HOCO internuclear distances. After some optimization the values  $\alpha_1$ = 2.0 bohrs and  $\alpha_2$  = 2.5 bohrs were chosen. This PI fit is denoted PI-1376. A second PI fit was also done. It consists of the subset of polynomials that contain only Ar-atom variables. There are just 79 such polynomials and so we denote this fit by PI-79. Also in this case, a single parameter  $\alpha = 2.0$ was used. This is clearly a substantial reduction in the number of terms and so should be more generally applicable. This is discussed further below.

Finally, the widely used pairwise-sum approximation was used as a fit. In this case, the interaction between Ar and each of the three types of atom in HOCO was approximated by a potential based on that proposed by Varandas and Rodrigues<sup>43</sup> and used by us earlier for a study of Ar and allyl radicals.<sup>36</sup> This pairwise potential (denoted Pairwise-18) is based on 18 parameters,<sup>44</sup> and it was determined by the FindFit routine in Mathematica<sup>45</sup> using a gradient method that provided an  $R^2 = 0.959$ .

All the potentials were fitted to the same set of  $12\,432$  UCCSD(T)-F12a/aVDZ counterpoise-corrected energies. The whole data set was generated by argon positions chosen along potential cuts of the distance of Ar to the HOCO center of mass and at various orientations and randomly scattered around different HOCO geometries including all stationary points on the HOCO PES. Additional random configurations were sampled from those visited along the paths of HOCO classically evolved trajectories at total energies of 12 000 and 20 000 cm<sup>-1</sup>. The distances between the argon

atom and the HOCO center of mass were chosen between 2.25 and 7.75 Å. Interaction energies up to 1.5 eV were considered. This ensures that the potential span regions that may be explored by the collision simulations we plan to perform. The interaction energy is calculated as the difference between the *ab initio* energies of the HOCO-Ar system and the two isolated moieties. We used a counterpoise correction to correct for basis set superposition error. The average counterpoise correction at the bottom of the wells along cuts is roughly 52 cm<sup>-1</sup> and we decided to keep it entirely.

In Table I the number of coefficients fitted, the total rms error, and its partition into 4 different energy regions are presented for the interaction potentials. The pairwise potential needed 18 parameters only, but it has a total rms error of 427.5  $\text{cm}^{-1}$ . This value is significantly lowered by means of a permutationally invariant fit. PI-79 gives an rms error slightly below 200 cm<sup>-1</sup>, while PI-1376 performs better than any other with the rms error of just 24.6 cm<sup>-1</sup>. Data relative to the rms error in different energy regions clearly demonstrate that the higher the energy, the more relevant the improvement in the accuracy in the case of PI-1376. In the highest energy range here considered, the rms error is more than 25 times lower for PI-1376 than for the pairwise potential. PI-1376 allows a much more reliable description of the bottom of the dispersion well as well as of the repulsive wall, which is of primary importance in energy transfer calculations.

We further tested the accuracy of PI-1376 by predicting energies for 3 potential cuts corresponding to 3 randomly chosen HOCO geometries. These cuts were made of a total of 50 ab initio points and were not included in the fit. The rms error of PI-1376 is increased to just 26.6 cm<sup>-1</sup>, thus confirming its high accuracy. PI-1376 will then serve as our benchmark potential in the preliminary energy transfer results we report below. Figure 1 shows potential curves obtained by using the potentials we have produced. Panel (a) is a prediction relative to ab initio energies not included in our database of 12432 fitted energies. Ab initio energies presented in panel (b), instead, were included in the database. PI-79 is less effective in describing the tail. On the other hand, it does better than the pairwise fit in the characterization of the dispersion well and the repulsive wall. Clearly, PI-1376 is free of all the drawbacks of the other fits and it is our preferred choice.

We report 6 contour plots in the supplementary material.<sup>44</sup> They describe the attractive part of the interaction potential in the molecular plane for both *trans* (left) and *cis* (right) isomers. PI fits (top and middle) present deeper attractive wells than Pairwise-18 (bottom), in agreement with rms error data. *Cis* and *trans* contour plots look similar for Pairwise-18, whereas the PI fits show a much stronger sensitivity to molecular geometry. This is also clear from an



FIG. 1. Comparison of accuracy of the different fits along potential cuts. z labels the distance between argon and HOCO center of mass. (a) A cut with *ab initio* energies not included in the database of 12 432 energies employed for the fits. (b) One of the cuts made of energies in the database. The HOCO geometries were randomly chosen between those visited during classical evolution of vibrationally excited HOCO.

analysis of the shape of the whole interaction region. PI-1376 features a shorter range of interaction, while PI-79, as expected, has characteristics in between the other two fits.

PI-1376 has been shown to be the most accurate fit, but different advantages are featured by other fits too. PI-79 relies on a smaller set of coefficients and so it is faster to use. Furthermore, not relying on internal HOCO distances, PI-79 is expected to be less sensitive when non-fitted distorted geometries are visited during trajectory evolution. The pairwise fits are even cheaper and always physically meaningful even for configurations where not enough *ab initio* energies have been generated. Practically, a pairwise potential could also be fitted to a much smaller set of points. According to the type of system under examination and its complexity, then, one would prefer to employ one kind of potential rather than another. Here, we perform some preliminary energy transfer calculations employing all the generated potentials. These simulations help us give an estimate of the importance of reproducing accurately the repulsive and attractive part of the potential. Results for PI-1376 are treated as the benchmark. They may help in future work for improvement of the pairwise potential.

Seven thousand HOCO-Ar trajectories were performed using each interaction potential, starting from the same identical initial conditions. The collision energy was set equal to 1 kcal/mol ( $349.7 \text{ cm}^{-1}$ ), the radical prepared in *trans* geometry with no angular momentum, and vibrationally excited by 9648 cm<sup>-1</sup>, so that the total energy was slightly below dissociation. We performed a microcanonical sampling of initial conditions, with excitation energy randomly distributed between the vibrational modes. The argon atom was initially positioned 15 a.u. away from the HOCO center of mass, far enough for the interaction to be considered negligible. The simulation was stopped when the argon atom was at a distance of 16 a.u. from the nearest HOCO atom. The impact parameters were extracted from the appropriate distribution by means of a Monte Carlo procedure. The maximum impact parameter ( $b_{max} = 11$  a.u.) was estimated from a small batch of runs following the procedure adopted in our previous work.<sup>36</sup> As may be estimated from Table II, less than 1% of collisions visited problematic configurations leading to unphysical dissociation of the molecule when using PI-1376. This very reduced ensemble of trajectories was discarded from the energy transfer analysis. The same table, after reporting the number of collisions resulting in energy transfers up and down, shows the average values per collision. The averages are referenced to the hard-sphere collision rate evaluated at  $b_{max}$ . Under the conditions of the simulation, energy is given to the molecule and a further inspection of the results shows that this energy goes into the rotational motion, while vibration is on average relaxed. In the case of PI-1376, the average vibrational

TABLE II. Collision data for the different fits. Collision energy is 1 kcal/mol (349.7 cm<sup>-1</sup>). HOCO is vibrationally excited with 9647.8 cm<sup>-1</sup>. Total energy is below dissociation.  $\Delta E$  refers to the change in total internal HOCO energy (rotational + vibrational).

	N <sub>up</sub>	N <sub>down</sub>	$\langle \Delta E^{up} \rangle$	$\langle \Delta E^{down} \rangle$	$\langle \Delta E^{tot} \rangle$	$\Delta E_{max}^{up}$	$\Delta E_{max}^{down}$	$\langle t \rangle$ (ps)	%HEC
Pairwise-18	6611	389	63.87	- 30.10	58.65	348.78	- 638.89	2.28	0.25%
PI-79	6182	818	90.27	-45.48	74.41	345.90	-1082.25	2.53	0.37%
PI-1376	5847	1085	95.51	- 46.23	73.33	344.77	- 1253.45	2.61	0.44%

energy loss is about 34 cm<sup>-1</sup>, while the average rotational energy gain is about 108 cm<sup>-1</sup>. Table II finally presents maximum values for energy transfers up and down, the average collisional time and the fraction of collisions which can be labeled as highly efficient collisions (HEC) according to Clary's criterion.<sup>46</sup> The average collisional (or simulation) time is the average of the total simulation time for the ensemble of all completed collisions. Collisions are labelled as HEC if their energy transfer is more than 5 times the average energy transfer down.

A data comparison points out that PI-79 provides results which are in good agreement with the benchmark ones, especially for the HEC fraction and maximum values of the energy transfer down which are strictly related to the repulsive wall. The number of collisions relaxing the molecule is also closer to the benchmark one. No trajectories needed to be discarded for PI-79.

The pairwise fit leads to reasonable and decent results, but our collision data confirm it lacks in accuracy for the repulsive part. The energy transfer down is not completely accounted for and the fraction of HEC is contracted. As a consequence of the shallower attractive part, the simulation time is reduced.

To conclude, we remark that our new Ar-HOCO PES is accurate and keeps computational costs affordable. It appears the most efficient way to treat Ar-HOCO collisions. Direct dynamics at the level of theory here employed is not feasible, since a single *ab initio* counterpoise-corrected energy takes about 20 min on a single core using MOLPRO, and an average trajectory is made of about 25 000 steps. The procedure we have followed to obtain PI-1376 is readily portable to other systems. A second, cheaper, PI fit has also been introduced. Preliminary results of energy transfer for this new potential are promising, since they are not far off the mark and we did not find any trajectories that had blown up before the collision was complete. This kind of restricted PI potential could be the preferred choice in the case of more complex systems. PI fits include multi-body contributions.

Finally, pairwise fitting has been shown to be still a quite reliable approach. It is the straightforward choice in complex systems or where a potential has to be obtained from just a handful of *ab initio* energies. PI-1376 results may serve as a model to improve the accuracy in the repulsive part of a pairwise fit. Recent calculations for water and HCl trimers<sup>47–49</sup> have demonstrated that at short distances three-body interactions, which cannot be accounted for by a pairwise potential, contribute relevantly. Molecular mechanics runs into similar troubles in dealing with the non-covalent, non-electrostatic part of the force field. However, our comparisons suggest that

different functional forms should be tested to better model the short range interaction. This is a possible goal of future research. The pairwise fit could be optimized to some observable like the benchmark energy transfer or the slope of the repulsive wall.

PI potentials are available upon request to the authors.

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- <sup>1</sup>J. R. Barker and D. M. Golden, Chem. Rev. **103**, 4577 (2003).
- <sup>2</sup>H.-G. Yu and J. S. Francisco, J. Chem. Phys. **128**, 244315 (2008).
- <sup>3</sup>J. S. Francisco, J. T. Muckerman, and H.-G. Yu, Acc. Chem. Res. **43**, 1519 (2010).
- <sup>4</sup>J. A. Miller, R. J. Kee, and C. K. Westbrook, Annu. Rev. Phys. Chem. **41**, 345 (1990).
- <sup>5</sup>B. J. Finlayson-Pitts and J. N. Pitts, *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications* (Academic Press, San Diego, 2000).
- <sup>6</sup>R. P. Wayne, *Chemistry of Atmosphere* (Oxford University Press, Oxford, 2000).
- <sup>7</sup>A. R. Ravishankara and R. L. Thompson, Chem. Phys. Lett. **99**, 377 (1983).
- <sup>8</sup>M. J. Frost, P. Sharkey, and I. W. M. Smith, Faraday Discuss. Chem. Soc. **91**, 305 (1991).
- <sup>9</sup>D. M. Golden, G. P. Smith, A. B. McEwen, C. L. Yu, B. Eitneer, M. Frenklach, G. L. Vaghjiani, A. R. Ravishankara, and F. P. Tully, J. Phys. Chem. A **102**, 8598 (1998).
- <sup>10</sup>M. Alagia, N. Balucani, P. Casavecchia, D. Stranges, and G. G. Volpi, J. Chem. Phys. **98**, 8341 (1993).
- <sup>11</sup>N. F. Scherer, C. Sipes, R. B. Bernstein, and A. H. Zewail, J. Chem. Phys. 92, 5239 (1990).
- <sup>12</sup>I. Ionov, G. A. Brucker, C. Jacques, L. Valachovic, and C. Wittig, J. Chem. Phys. 99, 6553 (1993).
- <sup>13</sup>J. Li, Y. Wang, B. Jiang, J. Ma, R. Dawes, D. Xie, J. M. Bowman, and H. Guo, J. Chem. Phys. **136**, 041103 (2012).
- <sup>14</sup>J. Chen, X. Xu, X. Xu, and D. H. Zhang, J. Chem. Phys. **138**, 221104 (2013).
- <sup>15</sup>A. M. Clements, R. E. Continetti, and J. S. Francisco, J. Chem. Phys. 117, 6478 (2002).
- <sup>16</sup>C. J. Johnson and R. E. Continetti, J. Phys. Chem. Lett. 1, 1895 (2010).
- <sup>17</sup>C. J. Johnson, B. L. J. Poad, B. B. Shen, and R. E. Continetti, J. Chem. Phys. **134**, 171106 (2011).
- <sup>18</sup>J. Ma, J. Li, and H. Guo, Phys. Rev. Lett. **109**, 063202 (2012).
- <sup>19</sup>X. Wang and J. M. Bowman, J. Phys. Chem. A **118**, 684 (2014).
- <sup>20</sup>J. Li, C. Xie, J. Ma, Y. Wang, R. Dawes, D. Xie, J. M. Bowman, and H. Guo, J. Phys. Chem. A **116**, 5057 (2012).
- <sup>21</sup>J. Ma, J. Li, and H. Guo, J. Phys. Chem. Lett. 3, 2482 (2012).
- <sup>22</sup>G. C. Schatz, M. S. Fitzcharles, and L. B. Harding, Faraday Discuss. Chem. Soc. 84, 359 (1987).
- <sup>23</sup>K. Kudla, A. Koures, L. B. Harding, and G. C. Schatz, J. Chem. Phys. 96, 7465 (1992).
- <sup>24</sup>K. S. Bradley and G. C. Schatz, J. Chem. Phys. 106, 8464 (1997).
- <sup>25</sup>F. N. Dzegilenko, J. Qi, and J. M. Bowman, Int. J. Quantum Chem. **65**, 965 (1997).
- <sup>26</sup>H.-G. Yu, J. T. Muckerman, and T. J. Sears, Chem. Phys. Lett. **349**, 547 (2001).
- <sup>27</sup>M. J. Lakin, D. Troya, G. C. Schatz, and L. B. Harding, J. Chem. Phys. 119, 5848 (2003).
- <sup>28</sup>R. C. Fortenberry, X. Huang, J. S. Francisco, T. D. Crawford, and T. J. Lee, J. Chem. Phys. **135**, 134301 (2011).

- <sup>29</sup>R. C. Fortenberry, X. Huang, J. S. Francisco, T. D. Crawford, and T. J. Lee, J. Chem. Phys. **135**, 214303 (2011).
- <sup>30</sup>C. J. Johnson, M. E. Harding, B. L. J. Poad, J. F. Stanton, and R. E. Continetti, J. Am. Chem. Soc. **133**, 19606 (2011).
- <sup>31</sup>M. Bruehl and G. C. Schatz, J. Chem. Phys. **89**, 770 (1988).
- <sup>32</sup>K. F. Lim and R. G. Gilbert, J. Phys. Chem. **94**, 77 (1990).
- <sup>33</sup>T. Lenzer, K. Luther, J. Troe, R. G. Gilbert, and K. F. Lim, J. Chem. Phys. 103, 626 (1995).
- <sup>34</sup>Z. Li, R. Sansom, S. Bonella, D. F. Coker, and A. S. Mullin, J. Phys. Chem. A 109, 7657 (2005).
- <sup>35</sup>A. Lombardi, N. Faginas-Lago, L. Pacifici, and A. Costantini, J. Phys. Chem. A **117**, 11430 (2013).
- <sup>36</sup>R. Conte, P. L. Houston, and J. M. Bowman, J. Phys. Chem. A **117**, 14028 (2013).
- <sup>37</sup>A. W. Jasper and J. A. Miller, J. Phys. Chem. A **113**, 5612 (2009).
- <sup>38</sup>A. W. Jasper and J. A. Miller, J. Phys. Chem. A **115**, 6438 (2011).
- <sup>39</sup>A. W. Jasper, J. A. Miller, and S. J. Klippenstein, J. Phys. Chem. A 117, 12243 (2013).
- <sup>40</sup>H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz *et al.*, MOLPRO, version 2010.1, a package of *ab initio* programs, 2010, see http://www.molpro.net.

- <sup>41</sup>B. J. Braams and J. M. Bowman, Int. Rev. Phys. Chem. 28, 577 (2009).
- <sup>42</sup>Z. Xie and J. M. Bowman, J. Chem. Theory Comput. **6**, 26 (2010).
- <sup>43</sup>A. J. C. Varandas and S. P. J. Rodrigues, J. Chem. Phys. **106**, 9647 (1997).
- <sup>44</sup>See supplementary material at http://dx.doi.org/10.1063/1.4871371 for values of Pairwise-18 parameters and contour plots.
- <sup>45</sup>Mathematica, Version 8.0, Wolfram Research, Inc., Champaign, IL, 2010.
- <sup>46</sup>C. D. Clary, R. G. Gilbert, V. Bernshtein, and I. Oref, Faraday Discuss. 102, 423 (1995).
- <sup>47</sup>Y. Wang, X. Huang, B. C. Shepler, B. J. Braams, and J. M. Bowman, J. Chem. Phys. **134**, 094509 (2011).
- <sup>48</sup>J. S. Mancini and J. M. Bowman, "A New Many-Body Potential Energy Surface for HCl Clusters and Its Application to Anharmonic Spectroscopy and Vibration–Vibration Energy Transfer in the HCl Trimer," J. Phys. Chem. A (published online) (2014).
- <sup>49</sup>J. S. Mancini, A. K. Samanta, J. M. Bowman, and H. Reisler, "Experiment and Theory Elucidate the Multichannel Predissociation Dynamics of the HCl Trimer: Breaking Up Is Hard To Do," J. Phys. Chem. A (published online) (2014).